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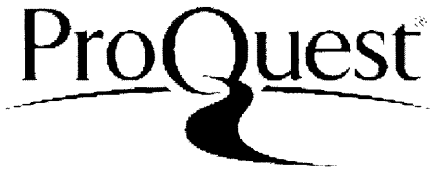
PASSIVITY OF TITANIUM WITH SPECIAL REFERENCE TO HYDROCHLORIC ACID SOLUTIONS

by
David Schlain

Thesis submitted to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy



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INTRODUCTION

According to Clarke, titanium makes up 0.62 percent of the lithosphere and is the tenth most abundant element. Only three structural metals, aluminum, iron, and magnesium are more abundant than titanium and it is more abundant than copper, lead, and zinc. Titanium is widely dispersed in the earth's crust and is generally present in igneous rocks and in the sedimentary material derived from them. Out of 800 igneous rocks analyzed in the laboratories of the United States Geological Survey, 784 contained titanium. It occurs most often as titanite, ilmenite, rutile and perofskite and does not occur free. The chief commercial mineral, ilmenite[24] ($FeTiO_3$), is found in many widely distributed deposits amenable to concentration. Large domestic deposits are available in New York, Wyoming, Virginia, Arkansas, and Florida. Substantial deposits of rutile (TiO_2) have been located in Virginia.

The use of titanium oxide in pigments is several decades old and has increased in recent years.[47] A new development is the electric smelting of ilmenite to produce pig iron and a slag with high, recoverable titanium dioxide content.[51] Titanium compounds also have minor industrial applications[33,52] and the tetrachloride has been used as a military smoke screen. But in spite of the availability of titanium compounds, the utilization of the metal as a structural material is just beginning. The high melting point of

titanium and its great affinity for nitrogen, carbon, and oxygen at high temperatures make it difficult to prepare in ductile form, and the unattractive physical data obtained by early investigators working with impure metal failed to reveal its possibilities.

Development of a commercially practical method for producing ductile titanium began about 1938 and eventually resulted in the production of titanium powder in 100 pound batches in the pilot plant at Boulder City, Nevada[60] and in making several tons of titanium metal available to various industrial and government laboratories for testing and development purposes. Realization of the potential value of titanium followed, and tremendous interest and activity began. According to Fontana,[20] the number of organizations working on titanium increased from four to sixty between 1946 and 1948. Another source[51] estimates that 10 million dollars have been spent on titanium research in the past three years. The work done in recent years includes not only investigations of the properties of titanium and its alloys and their fabrication, but also additional research on the production of the metal itself. Although the interest of the armed forces stimulated much of this work, commercially pure metallic titanium appears to be more than a defense development. In fall, 1950 annual production was 60 tons and observers predict a large increase by late 1951. Titanium is now being sold as sheet, strip, bar, rod, forging billet, and forgings.

DEVELOPMENT OF METALLIC TITANIUM

White titanium oxide was discovered by Gregor in a black magnetic sand found in Cornwall, England. Five years later Kisproth extracted the same oxide from Hungarian rutile and named it titanium. Kisproth, Lampadius, Berzelius, Wohler, Moissan, and others made many attempts to deposit this metal. These efforts sometimes resulted in hard, brittle, unworkable mixtures of nitrides, carbides, or cyanonitrides which because of their metallic luster were often mistaken for the element.[2,63] Hunter[36] was probably the first worker to prepare metallic titanium of reasonable purity. After trying various procedures without success, he was finally able to prepare metallic titanium by reducing titanium tetrachloride with sodium in a bomb exercising extraordinary care to exclude air from the apparatus during and after the reduction. Analyses indicated that the metal contained about 100 percent titanium. It had the appearance of polished steel and was hard and brittle in the cold but could be forged at low red heat. Attempts to produce wire from it was unsuccessful. Its specific gravity was 4.5 and melting point 1800 to 1850°C.

Several successful small-scale methods for the preparation of pure, ductile titanium were developed during the first three or four decades of the twentieth century. Van Arkel and De Boer[2] described a cyclic process which involved the formation of volatile titanium tetraiodide by

reacting crude titanium with iodine in the absence of other reactive gases, and depositing titanium on a hot tungsten wire by thermal decomposition in the upper part of the glass vessel. Recently, the process has been improved by the use of metal containers, titanium filaments etc.; iodine may be replaced by bromine.[6,29,30,31] Total impurities in metal made in this way have been estimated at 0.2 to 0.1 percent and include 0.05 percent tungsten, .01 to .05 percent silicon, and sometimes .01 to .1 percent iron. Other investigators[42] have reported other impurity contents, but oxygen, nitrogen, carbon, and hydrogen always seem to be absent. Kroll[38] reduced titanium tetrachloride with pure magnesium in a molybdenum-lined crucible in a pure argon atmosphere at 1000°C, washed the mass with water, hydrochloric acid etc., compressed the powdered titanium metal into bars and melted them in a vacuum. The metal could be rolled cold and made into wire.

The U. S. Bureau of Mines undertook an investigation into the technology of titanium in 1938 and after careful evaluation of virtually all known methods for the preparation of ductile titanium, Bean and his associates[10] selected the Kroll process as the most practical for large-scale operations. Although the Van Arkel process gives a product of greater purity it was found to have a number of defects. In the first place, it requires impure metallic titanium as a raw material; second, it would be difficult to use in large-scale production; and third, the metal is produced in

rods which cannot be melted for alloying without contamination. The development of the Kroll process was started in 1942 and the amount of metallic titanium produced per run increased in steps from a few grams to 100 pounds.[8,60] Each step in the process was studied critically with a view toward simplification and improvement of the product. The use of an unlined reaction vessel, more efficient removal of the titanium sponge from the vessel, and better methods for the elimination of residual magnesium and magnesium chloride from the sponge were among the changes made. The titanium powder contained the following impurities: magnesium 0.4 to 0.5 percent, iron 0.03 to 0.12 percent, manganese 0.02 to 0.15 percent, silicon 0.01 percent, chlorine 0.15 percent, hydrogen 0.06 to 0.3 percent, nitrogen 0.005 to 0.02 percent, and small amounts of oxygen, aluminum, phosphorus, sulfur, vanadium, and lead. It was found that of these impurities, gas believed to be absorbed on the surface of the powder had the greatest effect upon the mechanical properties of the titanium metal. The presence of 0.25 percent oxygen or 0.05 percent nitrogen caused the final metal to be brittle and unworkable. Hydrogen caused more embrittlement than oxygen but less than nitrogen. The hydrogen is easily removed (together with the magnesium) by sintering the powder at 1000°C in high vacuum. But nitrogen and oxygen form permanent solid solutions of the nitride and oxide which cannot be decomposed with sufficient completeness to restore the inherent ductility of the metal. It is

therefore essential to keep the hot metal from contact with these elements. Dean and his associates[8] concluded that powder metallurgy techniques offer the best possibilities for the consolidation of the granular product of the reduction. The high melting point of titanium and its great reactivity made available refractories inadequate for melting and casting methods. The Kroll method of melting mentioned above did not seem to be adaptable to much larger quantities of metal. The technique finally established involved pressing the powder into compacts at a pressure of 50 tons per square inch and sintering at 1000°C, in a vacuum of 1×10^{-4} millimeters of mercury. Other methods for consolidation of the powder and various aspects of the fabrication of the metal were also studied.[8,9,11,43]

In September, 1948 an industrial concern[a] announced plans for the commercial production of metallic titanium. Adopting the Kroll process but not the powder metallurgy technique, it embarked on a program of research on methods of melting the metal and casting it into ingots. This work and that of other organizations resulted in feasible induction melting[4,25,54] and arc melting[53] techniques with argon atmosphere. No completely satisfactory refractory[5] has been discovered but a graphite crucible has been used in the induction melting with some success. It results in metal which contains from 0.25 to 1.0 percent carbon and can

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[a] E. I. de Pont de Nemours and Company, Wilmington, Delaware.

be forged and rolled under proper conditions.[23] Tungsten or carbon electrodes and a water-cooled copper mold have been used in the arc melting. By 1950 this concern was producing 400 pound induction melted ingots and 50 pound arc-melted ingots. An affiliated company[a] is conducting research and development work on the fabrication of titanium and titanium alloys. Another industrial group[b] is using a modified Kroll process for the reduction to metal and is consolidating the metal by arc-melting in a water-cooled copper crucible with an inert-gas atmosphere.[56] It is planned to have 1000 pound ingots in regular production before the end of 1950. A commercial process for producing titanium metal from titanium dioxide by reduction with natural gas[12] has also been reported. In 1947 an industrial organization[c] announced a satisfactory method for producing ductile titanium from titanium dioxide but has released no further details.[51]

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[a]The Remington Arms Company, Bridgeport, Connecticut.

[b]The Allegheny Ludlum Steel Corporation and the National Lead Company.

[c]Dominion Magnesium Company, Canada.

PROPERTIES OF TITANIUM METAL

Some Chemical Properties

As much of the early work on titanium was done with impure metal, many discrepancies appear in the literature. The information briefly summarized below was compiled from several sources.[2,8,33,46,55]

Titanium is in Group IV A of the periodic system with zirconium, hafnium, and thorium and is the least metallic of these elements. Its atomic weight is 47.90 and its atomic number is 22. Titanium is the second member of the first transitional series of elements, including those from scandium (21) to zinc (30) in which the 3d orbits are being filled in preference to 4p orbits. Hence titanium has valencies 2, 3, and 4, and forms colored ions.[14] Quadrivalent titanium salts are easily hydrolyzed. According to its standard electrode potential, for which Latimer[40] gives a calculated value of 1.75 volts,[a] titanium comes between beryllium and magnesium in the electromotive series and should be a very active metal. In studying the tendency of titanium to replace metals from solutions of their salts, Botts and Krauskopf[3] found that the single electrode potentials of titanium in 0.25M solutions of trivalent chloride and sulfate were -0.23 volt and -0.18 volt,

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[a] $Ti = Ti^{++} + 2e \quad E^{o} = 1.75$ volts.

respectively versus the standard hydrogen electrode. A trace of hydrofluoric acid made the potentials 0.22 volt more electronegative while hydrochloric and sulfuric acids when added to the salt solutions caused the potentials to become more electropositive. In replacement experiments titanium acted like a less active element than the measured electrode potential indicated it should be. These investigators mentioned having difficulty in reproducting results and there is some doubt about the condition of the metal surfaces. At any rate, titanium is relatively inactive at room temperature but quite active at higher temperatures. Ordinarily, it does not react appreciably with oxygen below 120°C but does ignite in oxygen at 610°C and in air at 1200°C. Very finely divided titanium is pyrophoric, but even 35 mesh material is quite stable at room temperature. Titanium wire under 0.01 inch in diameter can be ignited in a Bunsen burner flame, but in larger sizes oxide scale forms on the surface of the wire without ignition. Although titanium does not react with nitrogen at room temperature, it burns with incandescence in nitrogen at 800°C forming hard, bronze-colored, metallic looking TiN. Another nitride, Ti_3N_4, has also been reported. Titanium also forms a nitride when heated with ammonia and a carbonitride when heated with carbon and nitrogen. Titanium combines with hydrogen at 500°C to give hard, brittle TiH_4, and powdered titanium decomposes steam at 700° of 800°C to give the oxide and hydrogen. The absorption of relatively small amounts of

hydrogen, oxygen, or nitrogen by titanium causes the metal to become brittle. The absorption of hydrogen is reversible, the gas being easily removed by heating the metal in a vacuum for a short time. On the other hand, oxygen or nitrogen form solid solutions of oxide or nitride which cannot be decomposed sufficiently to restore the ductility of the metal. At elevated temperatures titanium reacts directly with sulfur, phosporus, carbon, boron, and silica. It combines directly with halogens at temperatures varying from room temperatures for fluorine to 300°C for chlorine and 400°C for iodine.

Corrosion Properties

The literature contains a limited number of corrosion data for titanium virtually all of which are weight loss or visual observations made during standardized tests. The work described below was done in several laboratories, some of it with titanium compacted by powder metallurgical methods and some with melted metal. Although one might expect such factors as method of consolidation, heat treatment, fabrication procedure, and purity to influence the corrosion characteristics of a metal, the two types of metal do not exhibit significant differences. Perhaps the data now available are too few in number to reveal any except major differences.

Gee, Golden, and Lusby[22] studied the corrosion of titanium totally immersed in serated solutions of sulfuric

acid, hydrochloric acid, and nitric acid of various concentrations and at several temperatures. They used metal prepared in U. S. Bureau of Mines laboratories, compacted and sintered in the usual way, cold rolled to 40 percent reduction, and usually annealed at 1000°C for 1 hour. The final sheet was 0.04 inch thick and contained the following impurities: iron 0.1 percent, chromium, lead, magnesium, manganese, and copper 0.005 to 0.05 percent, nitrogen and oxygen present but not determined. They found that at 35°C annealed titanium was attacked rapidly by sulfuric acid in all concentrations above 5 percent and that the corrosion rate reached a maximum at 40 percent acid, dropped to a minimum at 65 percent, and then increased to 96.5 percent. Cold rolled titanium had higher corrosion rates than annealed titanium in 10 to 20 percent sulfuric acid solutions but there were no appreciable differences at other acid concentrations. When the metal corroded it did so without pitting. In similar experiments carried out for purposes of comparison 316 stainless steel resisted active corrosion in solutions containing up to 25 percent sulfuric acid. Annealed titanium has good resistance to hydrochloric acid solutions in concentrations up to 5 percent at 35°C., up to 3 percent at 60°C. and up to 1 percent at 100°C. Stainless steel corrodes rapidly in 5 percent acid at 35°C. and in 1 percent acid at 60°C. At 35°C. annealed titanium is very resistant to nitric acid in all concentrations up to 69.5 percent; it is particularly resistant in fuming acid

(90 percent) at room temperature. Five and 10 percent solutions of nitric acid corrode titanium slightly more at 100°C. than they do at 35°C. and 65 percent acid at 165°C. (the boiling point) results in only a small additional increase in the corrosion rate. Type 316 stainless steel exhibits similar corrosion properties in nitric acid except that in 65 percent acid at 165°C. its corrosion rate increases sharply. These workers found that titanium is quite resistant to 20 percent hydrochloric acid if it contains about 1 percent nitric acid. Kroll[39] obtained similar results with small additions of nitric acid. Gee and his associates[22] also indicate that titanium is resistant to boiling glacial acetic acid, 10 percent sodium hydroxide solution and to sea water. This work indicates that titanium is comparable to Type 316 stainless steel as a corrosion resistant metal in hydrochloric and nitric acids but is less effective than stainless steel in sulfuric acid. Titanium appears to be superior to alloy steel, monel, and nickel in their resistance to sea water.

Dean and his associates[8] present a few corrosion data for U. S. Bureau of Mines titanium in hydrochloric acid, sulfuric acid, nitric acid, 5 percent acetic acid, 5 percent ammonium hydroxide, and 5 percent sodium hydroxide solutions that are in substantial agreement with the data just summarized. These investigators also report that a dilute solution of sodium sulfide did not cause either a loss in weight or a discoloration of the surface and that exposure

of cold-worked or annealed specimens of titanium to salt spray for 30 days did not result in visible attack and or affect the tensile properties of the metal.

Williams[62] reports that titanium has great resistance to sea water after carrying out standardized corrosion tests on the Severn River and at Kure Beach. Fouling tests made in sea water at Wrightsville Beach, North Carolina indicate that titanium is not resistant to fouling organisms but that the metal beneath the fouling organisms does not corrode. This author also reports that specimens exposed to the atmosphere at Kure Beach quickly developed rust which is attributed to iron picked up in rolling the titanium sheets. Tests in which specimens were rotated at 27 feet per second for 19.5 days in water saturated with oxygen at 500°F and 700 pounds per square inch showed a small gain in weight for titanium and large losses in weight for 2S and 72S aluminum. The titanium specimens were slightly discolored at the end of the tests.

Fontana's[20] conclusions on the corrosion properties of titanium in sulfuric acid solutions disagree substantially with those of other investigators, possibly because of defective metal. His data indicate that titanium corrodes more than ordinary carbon steel in 65 or 93 percent sulfuric acid solutions and that titanium specimens show numerous pits after 168 hours of immersion in concentrations of sulfuric acid as low as 3 percent.

Hutchinson and Permar[37] studied the behavior of

commercially pure titanium in sea water and marine atmosphere exposures at the Marine Corrosion Test Station, Kure Beach, N. C. They used cold rolled sheet[a] produced by melting titanium metal sponge,[b] casting an ingot, and forging and rolling it to final thickness. The titanium sheet contained the following impurities: carbon 0.3 percent, oxygen, nitrogen, iron 0,02 percent to 0.2 percent each, other elements present in traces. They conclude on the basis of data obtained in tests 30 to 120 days in length with such standardized procedures as sea-spray test rack, marine atmosphere test lot, basin, sea-water overflow-discharge trough, aspirator-type jet-impingement apparatus, and high-speed galvanic tester that titanium is equal to such materials as Hastelloy C[c] and Stellite[d] in corrosion resistance. There was negligible overall attack and the metal showed no tendency to impingement attack, pitting, or crevice corrosion. Data obtained in the galvanic tester indicate that titanium, with an average steady-state potential of -0.15 volt (versus saturated calomel electrode) in sea water at 25°C flowing at 12 feet per second, is near

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[a]Made by Remington Arms Company, Bridgeport, Connecticut.

[b]Made by E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

[c]Approximate composition: nickel 59 percent, molybdenum 17 percent, iron 5 percent, chromium 14 percent, tungsten 5 percent, carbon 0.1 percent.

[d]Major constituents: cobalt, chromium and tungsten or molybdenum. Minor constituents may include carbon, iron, manganese, silicon, and nickel.

the inactive end of the La Que and Cox galvanic series of metals and alloys. A partial list of the metals in this series is as follows: tin, copper, nickel (passive), inconel (passive), titanium, monel, 18-8 stainless steel (passive).

Hutchinson and Permar also report the results of a long series of laboratory tests carried out at various temperatures and according to accepted procedures. There was no mechanical agitation; the vessel was open to the atmosphere but there was no provision for aeration. These data are in general agreement with those of Gee and his associates regarding the corrosion characteristics of titanium in hydrochloric, nitric, and sulfuric acids. When corrosion occurs, the action is "general"; corroded surfaces are uniform in texture, without areas of localized attack. No intergranular corrosion was observed, but there was the end grain attack common with rolled metals under severe conditions. The corrosion resistance of titanium appears to be a matter of extremes. The metal is either practically unaffected or it corrodes rapidly. There were borderline passivity phenomena in some solutions, one being boiling 50 percent formic acid. This probably occurs because the corrosion resistance of titanium is dependent on an effective protective layer. Such reagents as hot chromic acid and hot ferric chloride did not corrode titanium; boiling saturated sodium chloride, 10 percent zinc chloride, boiling 28 percent calcium chloride and sodium hypochlorite

at room temperature did not cause measurable weight loss or dull the brightness of the metal surface. Boiling 40 percent cupric chloride and boiling 10 percent ferric chloride, which are extremely corrosive to stainless steels, did not corrode titanium. Strong alkalis, such as boiling 10 percent sodium hydroxide and 10 percent sodium sulfide, resulted in moderate corrosion and 40 percent sodium hydroxide at 80°C caused accelerated corrosion. Ammonium hydroxide at room temperature did not cause a weight loss or change in appearance. Titanium also resisted boiling glacial acetic, acetic anhydride at 20-25°C, 30 percent chloroacetic acid at 20-25°C, and stearic acid at 180°C. The following reagents corroded titanium in excess of 0.005 inches per year: boiling 50 percent formic acid, hydrofluoric acid, 85 percent phosphoric acid at 25°C, boiling 10 percent phosphoric, 5 percent hydrochloric acid at 25°C, boiling 1 percent hydrochloric acid, 5 percent sulfuric acid at 25°C and 1 percent sulfuric acid at 80°C. It is suggested that titanium has improved corrosion resistance in oxidizing environments and there are data that indicate that nitric acid or air decrease corrosion in sulfuric or hydrochloric acids.

Data on the corrosion properties of iodide-deposited titanium are not available in the literature.

Physical Properties

Some of the important physical properties of cold-worked and annealed titanium made by the magnesium reduction and the iodide process are summarized in Table 1.

Table 1. Properties of Metallic Titanium[8,10,29,42]

	Magnesium Reduction		Iodide Process	
	Cold-worked[a]	Annealed[b]	Cold-worked	Annealed
Tensile strength, lb. per sq. in.	126,000	82,000	107,000	32,000
Yield strength, lb. per sq. in.	100,000	62,000	90,000	17,500
Proportional limit, lb. per sq.in.	72,000	55,000		
Elongation, per cent in 2 inches	4	28	2.5	55
Young's modulus, lb. per sq. in. x 10^6	15.4	16.8	16.2	11.2
Hardness, Rockwell A	A 65	A 55	B 38	
Melting point, °C	1725			
Electrical resistivity, ohms per cu cm. x 10^6	56		42	
Density, grams per c.c.	4.5		4.507	
Crystal structure Up to 880° 20°C hex.C.P. Above 880°C B.C.C.	a = 2.95 c = 4.73 a = 3.32		a = 2.946 c = 4.686 a = 3.32	
Specific Heat, Cal per gm per °C	0.13			

[a]Cold-worked - reduced 50 percent after annealing

[b]Annealed 2 hours at 800°C after cold working

The data for magnesium reduced titanium are for metal compacted by powder metallurgy methods but the values for melted titanium are substantially the same.[50] Iodide process titanium is much more pure than magnesium reduction metal. This greater purity results in a metal which is softer, has less strength and different electrical resistance. Whereas commercially pure metal can only be cold reduced 30-50 percent, high purity titanium can be cold reduced 99 percent. As is the case with many metals, cold rolling titanium greatly increases its strength and hardness without completely destroying its ductility. Complete annealing should be carried out in vacuum, since oxygen absorption is appreciable because of the formation of an oxide at 750°C. Beta titanium absorbs oxygen rapidly at temperatures over 880°C. However, rapid annealing in air is possible and permits additional cold rolling.

Titanium alloys very readily with other elements,[33,46] and much research is now in progress in this field.

The surface of ductile titanium can be hardened by heating it in a controlled atmosphere containing small amounts of oxygen and nitrogen. Experimental work indicates that 1.3 milligrams of oxygen per square centimeter of titanium surface produces a layer that appears to be solution of TiO in Ti and has a hardness of Rockwell C 58 at 0.04 millimeter below the surface.

POTENTIAL USES FOR TITANIUM

In evaluating titanium as a structural metal, its properties are frequently compared to those of aluminum alloys and stainless steel.[10,56] The density of titanium is between that of iron (7.9) and aluminum (2.8) and its melting point is higher than that of either. Its thermal and electrical conductivities are approximately the same as those of 18-8 austenitic stainless steel and are much lower than those of aluminum while its coefficient of thermal expansion is lower than that of either metal. Young's modulus for titanium is less than that of 18-8 austenitic stainless steel and more than that of 75 ST aluminum (a high strength aluminum alloy containing zinc, magnesium, and copper as major constituents). Annealed titanium has high yield strength with good elongation compared to 18-8 stainless steel in the same condition. Titanium compares favorably with either stainless steel or 75 ST on a strength-weight ratio basis. Massive titanium can be exposed to air at temperatures up to 1300°C without excessive embrittlement and although its strength decreases with rise in temperature, it should be useful as a structural material at temperatures up to 800°C. Aluminum alloys are not usually used at temperatures over 400°C. Available information indicates that titanium has good working properties. The fact that it can be surface hardened gives titanium an advantage over aluminum for frictional wear. Titanium is superior to both stainless

steel and aluminum in proportional limit, being comparable to the much heavier heat-treated steels and aluminum bronze.

Pure titanium metal is said to creep, that is, to fail slowly under load. Fatigue resistance and damping capacity are reported to be low, although melted metal is said to be better than powder metallurgy product. In spite of its high melting point, the usefulness of pure titanium at very high temperatures is limited by its low strength.

At present, titanium is very expensive. In the form of ilmenite it costs $.04 per pound, as titanium tetrachloride about $1.00 per pound, as titanium metal sponge[a] about $5.00 per pound, and as hot rolled and forged titanium bars[b] $6.00 per pound. An industrial organization[c] states[50] that it expects to "reduce the cost of titanium metal to a few dollars per pound within a few years with a prospect of further reduction". It seems reasonable to expect improved processes and large scale production methods to make this possible. Gee, Long, and Waggaman[24] point out that of a total cost of $5.25 per pound for titanium, 0.47 percent is ore cost and 99.53 percent is processing cost. They estimate an eventual cost of $.50 per pound. The corresponding figures for aluminum are $0.15 per pound, total cost and 99.34 percent processing, and for magnesium $0.20 per pound total

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[a]Du Pont, 1949.

[b]Titanium Metals Corporation 1950.

[c]Remington Arms Company.

cost and 90.35 percent processing. About 60 years ago aluminum and magnesium sold for $7.50 per pound and $10.00 per pound, respectively.

Titanium appears to have a unique combination of properties. It is superior to stainless steel in weight, to light metals in corrosion resistance, weight, and perhaps ease of surface hardening. It seems that most of the major uses for which it is now being considered are connected with the defense program. But large scale civilian uses should come as the cost decreases. The corrosion resistance of titanium will probably be important in the majority of its uses.

A FEW ELEMENTS OF CORROSION

Evans[17] defines corrosion as a transformation in which a metal passes from the elementary to the combined condition. Certain corrosion processes are not recognized as being electrochemical in character, as for example the rusting of iron in pure water with limited oxygen supply. Most instances of corrosion, however, are believed to be accompanied by the flow of electric current between anodic areas where metal atoms give up electrons and cathodic areas where the electrons take part in some reaction. An example frequently used to illustrate electrochemical corrosion is the process which occurs when a piece of iron covered with cracked mill scale is immersed in salt water. Iron dissolves in the exposed areas (anodic) according to this equation: $Fe = Fe^{++} + 2e$ The electrons flow to those portions of the metal covered with mill scale (cathodic) where they combine with molecular oxygen as follows: $\frac{1}{2}O_2 + H_2O + 2e = 2(OH)^-$ The ferrous and hydroxyl ions react to form ferrous hydroxide, usually at a point between the active areas. If sufficient oxygen is available the ferrous hydroxide is oxidized to a higher oxide of iron in hydrated form. Processes of this type are frequently rapid because the solid products are precipitated at a distance from the active areas and, therefore, cannot interfere with the reaction as the solid products frequently do in direct reactions. It has been shown experimentally that the quantity of metal dissolved in

electro-chemical corrosion is related by Faraday's law to the flow of current. The potential differences between areas on a piece of metal that result in electric currents and corrosion can be set up in various other ways, such as differential aeration or stresses.

The corrosion of a metal by a non-oxidizing acid is essentially the same as the process just described. Since the cathodic reaction now involves the elimination of hydrogen ($2\overset{+}{H} + 2e = H_2$) instead of the absorption of oxygen, the presence of oxygen is no longer necessary. When a metal is placed in contact with an acid the formation of metal ions and hydrogen molecules should proceed until the following equilibrium is established: $M + 2\overset{+}{H} \rightleftharpoons H_2 + M^{++}$. This will occur when the concentrations are such that the potential M/M^{++} equals potential $H_2/\overset{+}{H}$ at the surface of the metal. In the case of the noble metals at the positive end of the E.M.F. Series, this equilibrium will be established when the solution contains only a few hydrogen molecules, corresponding to a low hydrogen pressure in the gas space above. But in the case of metals with more electronegative electrode potentials, equilibrium will be reached at higher hydrogen pressures. If this equilibrium hydrogen pressure exceeds the total pressure on the gas space above the metal, the hydrogen will bubble or diffuse to the gas space, equilibrium will not be reached, the reactions will continue, and the metal will corrode. Even an electro-positive metal, such as copper, will corrode in boiling hydrochloric acid

because most of the dissolved metal is held in a complex ion and thus equilibrium is not established. The hydrogen-evolution type of corrosions differs from the oxygen-absorption type in that the cathodic reaction takes place in relatively small areas of low hydrogen overvoltage. The cathodic and anodic reactions may occur at contiguous points or even alternately at the same point. Some metals such as zinc, tin, and lead with electrode potentials that are quite electronegative do not corrode because high hydrogen overvoltages prevent the attainment of sufficient hydrogen pressure. Commercial zinc will corrode, however, since it contains impurities which dissolve, reprecipitate as sponge, and serve as cathodic areas. In attack by oxidizing acids, such as nitric, the cathodic reaction may be the reduction of the oxidizing agent, as for example the reaction of cathodic hydrogen and nitric acid to form ammonia, hydroxylamine, etc.

In electrochemical corrosion the anode and cathode processes must proceed at equal rates. The suppression of either reaction by such factors as the formation of a sparingly soluble salt on the metal surfaces, high hydrogen overvoltage, lack of oxygen, etc. retards the entire corrosion process.

When there is an appreciable flow of current through an electrolytic cell, it is no longer reversible and the electrode potentials change from their equilibrium values and are said to be polarized. Polarization results from the slowness of one or more of the processes occurring at the

electrode during the discharge or formation of an ion and the amount of polarization at an electrode generally varies with the current. If Figure 1 represents the corrosion of iron in dilute sulfuric acid, E_a and E_c are the reversible, equilibrium potentials of the electrodes Fe/Fe^{++} and H/H^{+} respectively, the lines E_a L and E_c L represent anode and cathode polarizations, and L represents the maximum current possible. If the resistance of the electrolytic path between anode and cathode is more than zero, the current is some value less than L, as represented by IR. Various factors affect the shape and slope of the polarization curves. Since massive cementite facilitates the cathode reaction, its presence in iron makes the cathode polarization curve less steep and this, in the absence of changes in the anode reaction, would raise the maximum current. The presence of sulfides in the iron results in the formation of hydrogen sulfide which makes the anodic polarization less steep and, if no change occurs in the cathode reaction, also raises the maximum current. In any one corrosion process there is likely to be a relationship between the corrosion potential and the current or corrosion velocity. This graphical method can, of course, be applied to other corrosion processes. A higher hydrogen overvoltage gives zinc a steeper cathode polarization curve than iron and a lower hydrogen overvoltage gives platinium a less steep polarization curve. In the corrosion of copper by sulfuric acid in the presence of oxygen, the cathodic reaction is the

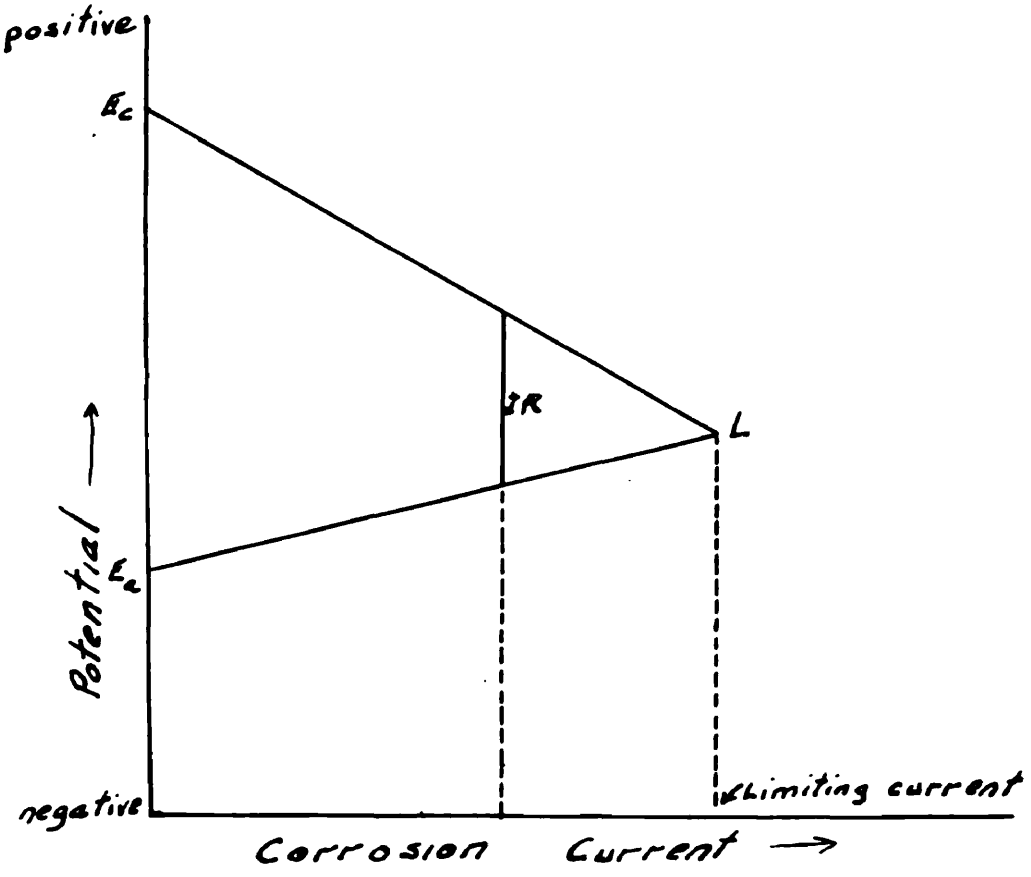


Figure 1 Current in Corrosion Cell [17]

conversion of oxygen to hydroxyl ions. The cathode polarization curve will be less steep and the corrosion rate will be higher in the presence of much air rather than little air. Complex forming reagents may depress the copper ion concentration and hence the potential of the copper electrode. Even though the cathodic curve is also depressed, slow corrosion with liberation of hydrogen may occur. Corrosion in oxidizing acids involves different cathodic reactions. These are more electro-positive, causing a higher initial potential difference and a higher corrosion rate. In the case of corrosion in neutral salts the cathodic reaction is probably the reduction of oxygen to hydroxyl ion. As the salt concentration increases, the resistance decreases and the corrosion current increases. But after a certain critical concentration, the corrosion current decreases with concentration because of higher cathode polarization caused by a decrease in oxygen solubility.

If, in a corrosion system of low resistance, the cathode polarization curve is much steeper than the anodic polarization curve, a change in the cathodic reaction has a big effect on the corrosion current while a change in the anodic reaction has relatively little effect. Such a system is said to be under cathodic control. If the anodic polarization curve is steep compared to the cathodic polarization curve the system is under anodic control and if both electrodes polarize in the same order of magnitude the system is under mixed control. If the resistance of the

electrolyte is large compared to the polarization at the electrodes, the system is under resistance control.

Galvanic corrosion[58] may occur when two dissimilar metals are in electrical contact in an electrolyte, and much that has already been said of electrochemical corrosion in general is true of galvanic corrosion. Contact will generally cause the anodic member (more electronegative) of the galvanic couple to corrode more and the cathodic (more electropositive) to corrode less than the normal corrosion. The current that flows between the two metals is called the galvanic current and that portion of the corrosion of the anode which is related to it by Faraday's Law is the galvanic corrosion. The simultaneous additional corrosion taking place on the anode is the local corrosion. When the galvanic corrosion causes a change in the normal corrosion of the anode, such a change is the difference effect. When the galvanic current reduces the total corrosion of the cathode, the reduction is called galvanic or cathodic protection and when the total corrosion is increased the increase is called cathodic corrosion.

PASSIVITY

Various Types

Many instances of passivity[59] in metals have been reported since the end of the eighteenth century when the inertness of iron in concentrated nitric acid was first observed. Passivity is not an absolute property but may be present in variable degrees and can be achieved by a variety of means. Oxidizing conditions, anodic polarization, or contact with a more noble metal are likely to favor passivity while reducing conditions, cathodic polarization or contact with a less noble metal tend to destroy it. Halogen ions, and particularly chloride ion, destroy passivity. In the case of metals such as chromium, aluminum, or stainless steel, chloride ion destroys passivity in relatively small areas. This results in cells with small, active anodic areas and large, passive cathodic areas and causes pitting. Alkaline solutions may be destructive to passivity of amphoteric metals such as aluminum or zinc. Elevated temperatures and even magnetic fields are said to destroy passivity, the evidence for the latter being inconclusive.

Various types of passivity are now recognized and they have been defined in several ways. Uhlig and Mears[58] define passivity as a property of a metal in two ways, as follows: (1) "A metal active in the E.M.F. series, or an alloy composed of such metals, is considered passive when its

electrochemical behavior becomes that of an appreciably less active or noble metal" (2) "A metal or alloy is passive if it substantially resists corrosion in an environment where thermodynamically there is a large free energy decrease associated with its passage from the metallic state to appropriate corrosion products." Eldredge and Warner[13] define an inhibitor as "any substance which when added in small amounts to the corrosive environment of a metal or alloy effectively decreases the corrosion rate." They define a passivator as an inhibitor which "when added to the environment of a metal or alloy appreciably changes the electrochemical potential to a more cathodic or noble value." Obviously, the second definition of Uhlig and Mears and the term inhibitor have the broader meanings and are probably used more widely.

Passivity by definition 1 is quite different from passivity by definition 2. Iron inactive in nitric acid (sp.gr. > 1,4) is passive by both definitions but amalgamated or pure zinc in dilute sulfuric acid is passive only by definition 2. Faraday is said to have been the first to point out that if platinum is brought into contact with the iron, little if any current will be produced whereas if platinum is brought into contact with the zinc, current normal for zinc will result. Iron in contact with passivators such as HNO_3 (sp.gr. > 1,4), $NaNO_2$, $K_2Cr_2O_7$, or Na_2FeO_4 as well as most transition metals and passive alloys such as stainless

steel, are frequently passive according to definition 1. In other words, the electrode potentials become appreciably more electropositive. For example, iron in 0.01 M $K_2Cr_2O_7$ is more than 0.5 volt more noble than iron in tap water. Passivity by definition 2 includes the examples just given and, in addition, cases of passivity involving chemical conversation coatings in which relatively thick films give protection in the manner of a paint film. Examples in this category are lead in H_2SO_4, zinc or aluminum in Na_2SiO_3, iron in conc. H_2SO_4, magnesium in H_2O or HF (> 2%) and silver in HCl. The metals in these cases undergo only slight changes in potentials as a result of becoming passive.

Evans[15] treats the subject somewhat differently and classifies inhibitors according to method of functioning, as follows:

(1) anodic inhibitors

(2) cathodic inhibitors

  (a) for oxygen absorption type of attack

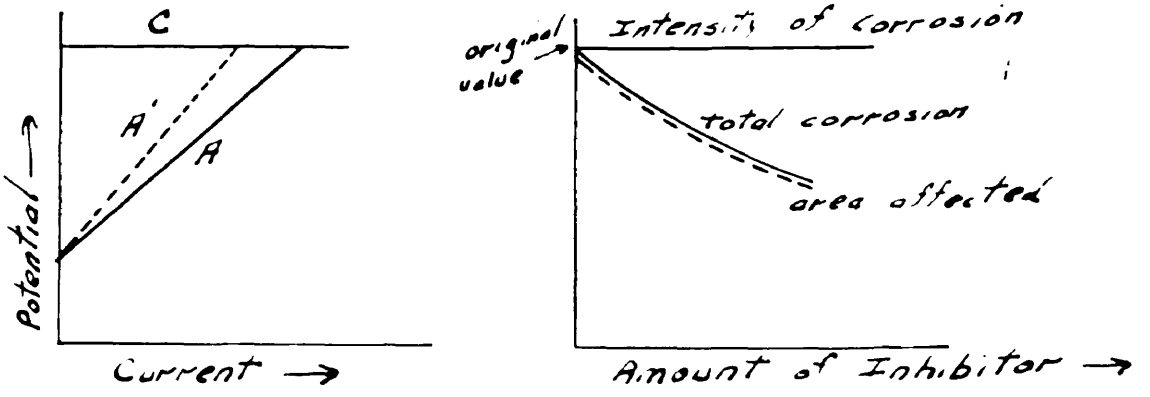
  (b) for the hydrogen liberation type of attack

(3) adsorption inhibitors

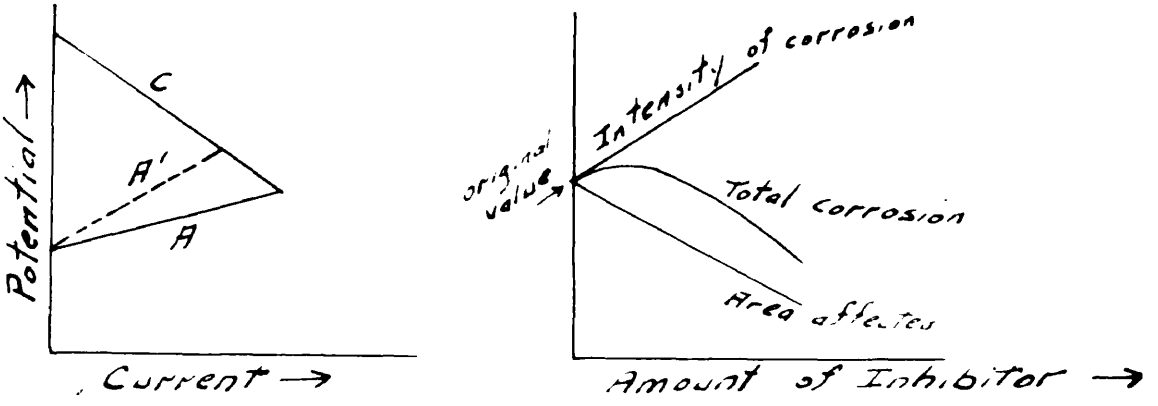
Some reagents act on both anode and cathode and some adsorption inhibitors act preferentially at anode or cathode areas.

Anodic inhibitors function by increasing the polarization of the anodic areas. They are frequently sodium or potassium salts with anions that form sparingly soluble salts with the

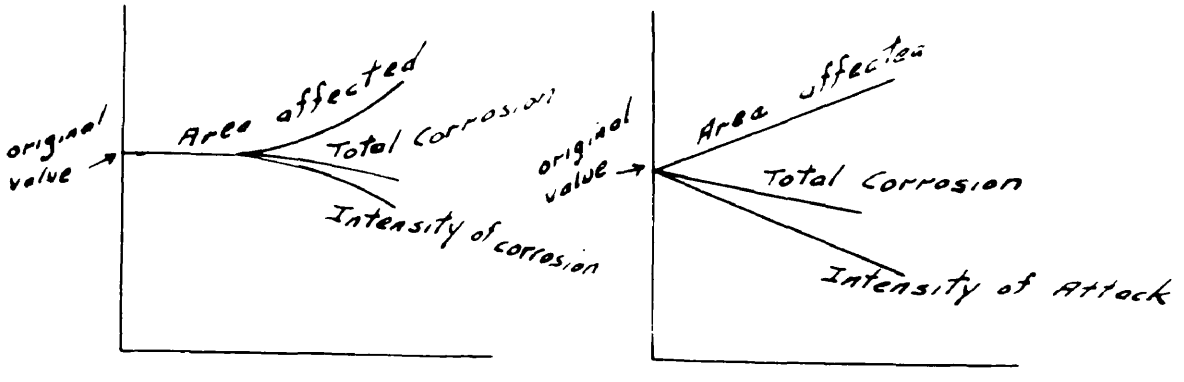
metal. Chromates, hydroxides, phosphates, or carbonates are frequently used for iron. Chromates are probably most effective, and function by repairing the original air-formed iron oxide-film at weak spots with a ferric-chromic oxide precipitate formed by interaction of ferrous iron and chromate under the proper conditions. Evans suggests that stainless steel receives its protection in the same manner. But the film on stainless steel is permanently self-repairing whereas iron loses its resistance within a day after removal of the chromatic solution. Heat, the presence of chloride ion, and to some extent the presence of the sulfate ion increase the amount of chromate necessary. In the presence of acid such as 0.05 M sulfuric, chromate may be a cathodic stimulator and increase the corrosion rate. Evans[16,18] provides an analysis of the effect of inhibitors on various corrosion systems. When an inhibitor is added to a system under anodic control (Figure 2, I) the anodic polarization curve becomes more steep, A to A'. If the original conductivity of the solution was high the final potential is unchanged and the current is decreased. This suggests that the current density and, therefore, the intensity of corrosion will remain the same and that the total corrosion and the area of corrosion will fall at the same rate. If an anodic inhibitor is added to a system under complete cathodic control it will have no effect unless it caused the control to shift. This seems likely to take place. But if the system



I Anodic Inhibitor and Anodic Control



II Anodic Inhibitor and Partial Cathodic Control



III Cathodic Inhibitor and Anodic Control

IV Cathodic Inhibitor and Cathodic Control

Figure 2 Effect of Inhibitors on Corrosion[16]

is under partial cathodic control (Figure 2, II) the anodic inhibitor will cause the anodic polarization to increase more rapidly and will raise the potential by a larger amount resulting in a higher current density and greater intensity of corrosion. The corroded area is reduced faster than the total corrosion. If control is predominantly cathodic the inhibitor, in small amounts, may increase the corrosion rate as well as the intensity by increasing the cathodic area. But as more reagent is added, the anode area becomes smaller, anode control increases, and the corrosion rate falls. Anodic inhibitors are more efficient than cathodic inhibitors but are considered dangerous because in insufficient amounts they can result in increased intensity of corrosion and thus result in early failure of the structure.

Cathodic inhibitors act by increasing the polarization of the cathodic areas. Inhibitors for the oxygen-absorption type of attack tend to isolate cathodic areas and lessen access of oxygen for the cathodic reaction. Salts of metals like zinc and nickel that form sparingly soluble hydroxides decrease corrosion of iron in neutral solutions in this manner. Inhibitors for the hydrogen-evolution type of attack seem to act specifically at cathodic points, apparently by raising the hydrogen overvoltage to a high value and decreasing hydrogen evolution. Mercury, antimony, and arsenic may inhibit corrosion by acid in this manner. The addition of a cathodic inhibitor to a corrosion system under anodic

control (Figure 2, III) has no effect until the original cathodic area is obstructed enough for partial anodic control to be initiated. Then the corrosion rate will decrease and, since the anodic area is increasing, the intensity of corrosion will decrease even more. Where a cathodic inhibitor is added to a system under cathodic control (Figure 2, IV) the total corrosion and the intensity of attack decrease for the reasons previously given. Since cathodic inhibitors do not generally intensify corrosion, they are referred to as "safe". A reagent may be an inhibitor for one metal and a stimulator for another. Nitrates inhibit attack on aluminum and are cathodic stimulators for iron.

Cathodic inhibitors generally form relatively thick, visible layers of material while anodic inhibitors result in films too thin to be visible. Cathodic inhibitors do not usually stop corrosion entirely but anodic inhibitors, in sufficient quantity, do. While anodic inhibitors may confer a more noble potential on a metal and make it passive according to definition (1) of Uhlig and Mears, a cathodic inhibitor is not likely to do this.

Adsorption inhibitors are organic substances of high molecular weight that function chiefly by shielding the surface and hindering contact with the corrodent. Some of these reagents may act preferentially at anode or cathode. Agar, egg albumen, and gum tragacanth are adsorption inhibitors.

The effect of oxygen on the corrosion rate may be

interesting. At ordinary pressures, oxygen increases the corrosion rate of iron in most neutral salt solutions but may diminish the probability of attack. At high pressures, oxygen is reported to be an inhibitor. It is an inhibitor, even at low pressures, in alkaline solutions. There are data to show that the passivity produced by sodium hydroxide, carbonate or phosphate requires the presence of iron. With materials like some chromium-nickel and iron-chromium-nickel alloys that seem to owe their resistance to protective films, oxygen is an inhibitor.

Theories of Passivity

Uhlig and Mears[59] briefly summarize the theories of passivity. Of the theories that have been suggested, the so-called film theory is the one most widely accepted today. It seems to have originated with Faraday who explained the passivity of iron in nitric acid by the formation of an oxide film. This was later generalized and most cases of passivity are now attributed, directly or indirectly, to protective oxide or similar films. It has been suggested that the passivity of iron, nickel, cobalt, and chromium is the result of a film of adsorbed oxygen. Adsorbed oxygen is known to be very inert, presumably because of the satisfaction of valence forces by the surface atoms of the metal. A film of adsorbed oxygen on tungsten does not react with hydrogen at 1200°C. If the adsorbed film is weakened by the reduction of oxygen pressure in the atmosphere

around the sample, it suddenly becomes reactive. The available evidence for the adsorbed oxygen viewpoint is not conclusive.

Various workers have suggested that there is a relation between the electron configuration of atoms and passivity. Uhlig[57,59] combined some of these ideas with the generalized film theory into the Electron Configuration theory which attempts to offer additional explanation for passivity (by definition 1) exhibited by metals and alloys. It is chiefly of interest with reference to alloys. The data presented in support of the theory are interesting but too few to be conclusive. Furthermore, data that fail to support the theory have been recorded.[57] The theory is based on the fact that metals passive according to definition 1 are generally in the transition group in the Periodic Table. The atoms of these elements (e.g. Cr, Ni, Co, Fe, Mo, W) are characterized by incomplete inner shell (d electron) energy levels and by unfilled energy bands in the metallic state. It is assumed that these unfilled energy states tend to become filled with electrons, just as closed atomic shells are the tendency in forming chemical compounds. Passivity is ascribed to unfilled d bands in the metal or alloy, and the active state to the situation that fills the d band with electrons. Adsorbed oxygen or adsorbed oxidizing substances impart maximum passivity because they are electron absorbers with no tendency to supply electrons to atoms of metal

covered with monatomic or monomolecular films and the presence of thicker films is unnecessary for passivity. Iron is passive in nitric acid because of an unstable higher oxide of iron produced by momentary reaction. This oxide is electron absorbing and is adsorbed on the surface of the iron. In stainless steels, naturally passive chromium has a strong tendency to absorb electrons and imparts passivity to iron by electron sharing. This seems to require at least one extra electron per iron atom. Evidence of this is the fact that active iron corrodes to Fe^{2+} whereas iron from stainless steel corrodes to Fe^{3+}. The electronic structure of chromium is such that each atom should be able to passivate 5 atoms of iron (16.7-15.7 percent chromium). This is in fair agreement with the observed critical minimum percentage of chromium necessary for passivity (12 percent chromium). Uhlig points out that the minimum chromium content, as experimentally determined, may increase in such non-oxidizing acid solutions as ferrous sulfate, and that the alloy is not passive in hydrochloric acid no matter what the chromium concentration. Uhlig has accounted for passivity in several other alloy systems in the same way.

According to this theory chromate or nitrate ions passivate iron by sharing electrons from surface iron atoms and forming an adsorbed layer on the iron. It satisfies secondary valence forces but does not disrupt the metal lattice. Hence the metal surface is less reactive and is passive by

definition 1. According to the film theory, chromate and nitrate act to form thin protective films composed of unsoluble iron compounds. Cathodic hydrogen is an activator by either theory. According to the film theory it acts by direct reduction of the protective film, but according to the Electron Configuration Theory it first adsorbs on or dissolves in the metal and changes the electron configuration of the metal atoms which, in turn alters the nature of the adsorbed surface films. Chloride ions destroy passivity, according to the film theory, by penetrating the film or colloidally dispersing it but according to Uhlig's theory, chloride ions act in the same way as hydrogen.

Uhlig points out that aluminum is certainly passive by definition 1 and yet is not a transition metal and has no place in his theory. The generalizations regarding the passivity of alloys of chromium, nickel, and molybdenum made by Uhlig are valuable and may make it possible to predict combinations of metals that will be passive. However, the theory does not add much to our understanding of the mechanics of passivity and there is yet little knowledge of the manner in which such passivators as oxygen and chromate function. The theory adds little to the commonly held belief that oxidizing agents frequently passivate and reducing agents frequently activate metal surfaces.

Monypenny[48] presents some interesting data on stainless steel. Steel containing 12.6 percent chromium and 0.3 percent

carbon, if placed in N nitric acid, corrodes at a decreasing rate and eventually action stops. He attributes this phenomena to the accumulation of ferric nitrate and notes that the addition of about 1.5 grams per liter of iron as ferric nitrate to the nitric acid before the test is started decreases the initial corrosion rate by 50 percent, and the addition of 5 grams of iron will eliminate corrosion entirely. Copper has the same effect; 1.5 grams of copper per liter will decrease the corrosion rate by 75 percent but it requires 8 grams to stop corrosion completely. Similar results are obtained with sulfuric acid solutions. In a solution containing 100 grams $CuSO_4 \cdot 5H_2O$ per liter there is no corrosion with 75 grams sulfuric acid per liter and rapid corrosion with 200 grams sulfuric acid per liter. If copper is added to sulfuric acid solutions containing 50 or 100 grams of acid per liter the rate of corrosion increases with copper concentration at first probably because the precipitation of copper as a flocculent mass sets up couples. The maximum corrosion rates occur at 5 grams of $CuSO_4 \cdot 5H_2O$ per liter for 50 grams acid per liter and 15 grams $CuSO_4 \cdot 5H_2O$ per liter for 100 grams acid. Then the corrosion rates decrease with increasing copper concentration. These effects seem to vary somewhat with composition of steel, hardness, etc. The metal ions do not decrease corrosion in hydrochloric acid and ferrous ion does not decrease corrosion in sulfuric acid. Apparently no electrode potential measurements were

made and hence it is not possible to say definitely that the stainless steel was passive by definition 1.

Uhlig explains the action of these metal ions according to his theory, but it seems difficult to explain the fact that such high concentrations of metal ions are necessary for an adsorption layer. Furthermore, the initial solution of stainless steel in N nitric acid suggests that the same phenomenon may occur much more rapidly in more concentrated solutions.

ELECTRODE POTENTIALS

Definition

The electrode potential or single electrode potential of a metal may be defined as the potential difference at the surface of separation between the metal and the electrolyte in contact with it. Electrode potentials may be thermodynamically reversible or irreversible, depending on whether or not they are part of reversible or irreversible galvanic cells. When the electrolyte contains the metal ions at unit activity the potential is the standard electrode potential of the metal (E°). The standard electrode potential of a metal may be related to its electrode potential at various other ion concentrations by the following equation:[26]

$$E_{\pm} = E^{\circ} \mp \frac{RT}{Z \pm F} \ln a_i$$

or

$$E_{\pm} = E^{\circ} \mp \frac{.05915}{Z \pm} \log a_i$$

Z is valence of metal ion; a_1 is the activity. The upper sign is used for positive ions and the lower sign for negative ions.

In this investigation electrode potentials will be referred to the hydrogen scale, that is the potential of the standard hydrogen electrode will be taken as zero. The

convention for signs will be such that the standard electrode potential of zinc ($1/2\ Zn = 1/2\ Zn^{++} + e$) will be -.762 volt and that for copper ($1/2\ Cu = 1/2\ Cu^{++} + e$) will be 0.345. This is the reverse of the convention advocated by the American Chemical Society but seems to be preferred by workers in the field of corrosion.

Measurement

Electrode potentials will be determined by combining the electrode (usually titanium in an electrolyte) with a saturated calomel electrode and measuring the electromotive force of the cell. The temperature coefficient of the saturated calomel electrode is almost ten times as large as that of the 0.1 N potassium chloride electrode but the saturated electrode is easy to set up, and when it is used in conjunction with a saturated potassium chloride bridge, one liquid junction is avoided. The measurements will be made at room temperature and even according to the temperature coefficient[a] given by Glasstone,[28] which is much greater than the earlier value of Fales and Mudge,[19] a variation of 5°C. from 25°C. changes the potential by only 0.0045 volt. The problem of liquid junction potentials is more difficult and will be discussed in more detail.

A liquid junction potential or diffusion potential is set up at the point of contact of two electrolytes because

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[a] Hg, Hg_2Cl_2(S) Sat.KCl Potential (referred to normal hydrogen electrode) equals 0.2415 - 0.00076 (t-25).

of differences in rates of ion migration. The use of a salt bridge to connect the two electrolytes minimizes this potential because the concentration of the salt is generally greater than that of the other electrolytes and hence it carries most of the current across the junction. Either potassium chloride or ammonium nitrate are effective because in each of these salts the two ions move with approximately equal velocity. The saturated potassium chloride bridge used in this investigation eliminated one junction entirely and, in some of the measurements, it should also decrease the potential at the other liquid junction. The available theoretical and experimental information do not permit accurate evaluation of the second junction potentials in some of the work. However, an attempt will be made to estimate the order of magnitude of the potentials at these liquid junctions, KCl (sat.) / Electrolyte.

It is known that the method of forming a liquid junction affects the value of the potential. Guggenheim[34] describes several types of junctions including free diffusion, constrained diffusion, continuous mixture layer, and flowing junction. He states that the junction potential for two concentrations of the same salt is independent of the method of forming the junction but that the nature of the junction is important when the salts are different. One method for handling the liquid junction problem is to make it reproducible and correct for it. A properly constructed flow junction[44] is believed to have the best reproducibility

Variations of several millivolts were obtained with various indefinite types of junctions.[34] Of the indefinite types, the junction within a tube seems best since it gives cylindrical symmetry of transition layer. Guggenheim proved that if the two electrolytes are 0.1 N HCl and 0.1 N KCl the junction potentials with a 3.5 N KCl bridge are only 1 or 2 millivolts with either continuous mixture or free diffusion types of junctions. The Lewis and Sargent equation has been suggested for estimating the liquid junction potential for 2 uni-univalent electrolytes at the same concentrations with a common ion when the junction is of the continuous mixture type. This is given in Glasstone[27] in the form

$$E_L = \frac{RT}{F} \ln \frac{\Lambda_1}{\Lambda_2}$$

(Λ_1 and Λ_2 are equivalent conductances of two electrolytes)

Using this equation, the liquid junction potential for 0.1 N KCl and HCl (without a bridge) was estimated at 28.5 millivolts and checked experimentally.[44] With the same formula and with equivalent conductance values from Perry,[49] the potentials for 1 N and 3 N solutions were estimated at 28 and 22 millivolts, respectively. Experimental evidence presented by Guggenheim indicates that the junction potential for concentrated KCl and dilute HCl is less than for solutions of equal concentration. Hence, the junction potential when using 1 N and 3 N HCl with a saturated KCl bridge should be less than the calculated values. Apparently the junction

potentials for very concentrated hydrochloric acid saturated potassium chloride solution cannot be calculated. The fact that the equivalent conductances for 3 N KCl and 10 N HCl are nearly equal is promising but may be misleading. The measurements made in sodium chloride solutions should involve relatively small liquid junction potentials since sodium chloride and potassium chloride solutions have smaller liquid junction potentials and the sodium chloride solutions are weak. There seems to be no way to estimate the potential for the junction KCl sat./$SO_4$2N. The measurements of the zinc electrode, Zn/Zn^{++}, indicated errors of 0.01 volt or less, but these measurements were made with sulfate solutions much less concentrated than 2 N. Hamer[35] studied junction potentials for various types of electrolytes when using a saturated calomel cell and a saturated potassium chloride bridge and his values for the potential of the saturated calomel electrode under these conditions indicate the size of the error due to junction potential. Some of these values are: true value sat. calomel cell 0.2435 volt, 1 N HCl with junction potential 0.2512 volt, 0.1 N HCl with junction potential 0.2431 volt, 0.01 N HCl with junction potential 0.2455 volt.

It seemed best to use the average value of 0.2457 volts for the saturated calomel electrode suggested by Hamer, to make no temperature or liquid junction corrections, and to round final values to the nearest 0.01 volt. This decision was made for the following reasons:

(1) Temperature errors at room temperatures are probably less than 0.005 volt.

(2) The liquid junction potential for 3 N HCl were estimated at 0.02 volts and may be somewhat less. Potentials for more concentrated HCl cannot be estimated but there is no reason to expect that they will be of a higher order of magnitude. Liquid junction potentials for more dilute hydrochloric acid solutions appear to be 0.01 volt or less and for sodium chloride solutions are even less.

(3) The value 0.2457 volt is an intermediate one and is only different by 0.004 volts from that suggested by Hamer for 1 N hydrochloric acid. Much of the work was done with 1 N hydrochloric acid.

(4) Accuracy of 0.01 volt is sufficient for this work and for most corrosion studies.

Significance of Electrode Potential

The electrode reactions in a corrosion process result in the dissipation of energy and, therefore, the electrode potentials are not reversible, equilibrium potentials. However, if the electrode reactions take place at a constant rate the electrode potential of the corroding metal reaches a steady-state value which is reproducible and may be called the corrosion potential. The electrode potential of a metal in an electrolyte, if correctly interpreted, may indicate its tendency to corrode, but it is not generally useful in predicting corrosion rates.

Time-potential curves can be very valuable in corrosion studies. Evans[17] points out the relationship between change of potential with time and passivity. If a specimen of metal with an oxide film is placed in a salt solution, the areas covered with film become the cathodes and the defective film areas become the anodes of the corrosion cells. Cathodic and anodic polarization takes place as indicated in Figure 3, the current "i" assumes a value such as to produce the intercept "iR", and the electrode potential of the metal specimen becomes P. If the solution is such as to repair the film or promote passivity, the anodic area shrinks, the anodic polarization curve becomes more steep, the resistance increases, the current decreases, and the electrode potential of the specimen becomes more electropositive. But if the solution destroys the film and promotes corrosion, the anodic area becomes larger, the anodic polarization curve becomes less steep, the resistance decreases, the current increases, and the measured potential becomes more electronegative. Evans[16] also points out that a cathodic inhibitor could cause the electrode potential of the metal specimen to become more electronegative. However, this is not common.

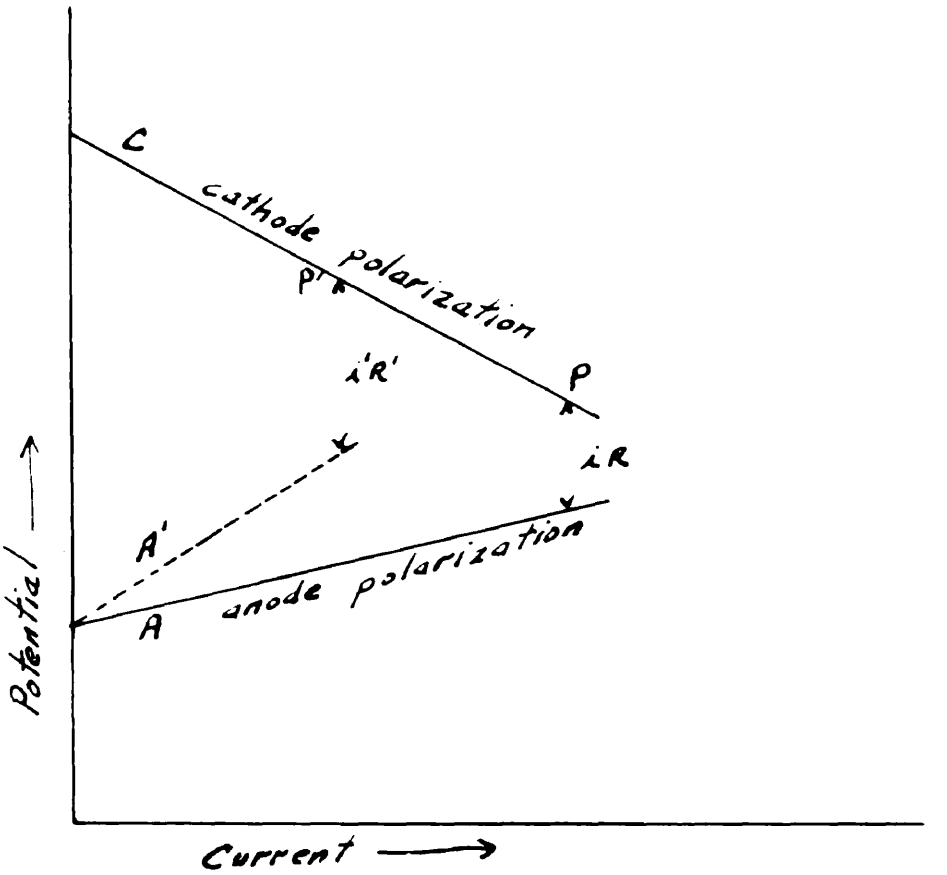

Figure 3 Electrode Potential of Metal [17]

PRESENT INVESTIGATION

The potential value of titanium as a structural metal depends on its low density, high strength, and good corrosion resistance. Corrosion resistance is probably the key property of the combination. The available data on the behavior of titanium in nitric acid and its chemical inertness at low temperatures relative to its position in the electromotive force series indicate a tendency toward passivity. Furthermore, its position in the first transition group of elements is interesting in the light of Uhlig's theory with respect to the passivity of the third transition group. Since the passivity of titanium is undoubtedly fundamental to its chemical and galvanic corrosion behavior, this investigation will be concerned with certain aspects of this property.

Electrode potential measurements appear to be a promising approach to the study of the fundamentals of passivity. Since only weight loss data and a few potential measurements of limited usefulness are now available, it will be necessary to carry out considerable exploratory work on titanium before the field of investigation can be defined further.

PRELIMINARY EXPERIMENTAL WORK

Several groups of experiments were carried out to investigate the behavior of titanium in contact with electrolytes under various conditions, to study equipment and experimental procedures, and to obtain necessary information about certain other metals.

C.P. chemicals, distilled water, and commercially pure metals were used in all experiments. The titanium metal was prepared in Bureau of Mines laboratories. Electrode potentials were measured with an L and N type K-2 potentiometer a saturated calomel electrode, and a saturated potassium chloride bridge. As a check on the accuracy of these determinations, the electrode potential of zinc was measured in several concentrations of zinc sulfate. After correcting the standard electrode potential of zinc for concentration, the measured values were always within 0.01 volt of the theoretical value. The standard cell (Eppley) was also compared with another standard cell and found to be in close agreement. For the reasons presented earlier, the value +0.246 volt was used for the potential of the saturated calomel cell with reference to the standard hydrogen electrode, no temperature corrections were made, and the electrode potential values were given to the nearest 0.01 volt. Some of the electrode potential measurements, as for example those in sodium chloride solutions or in 1 N hydrochloric acid solutions, could probably be given to the nearest 0.001 volt but the extra significant figure is not necessary in this investigation.

Single Electrode Potentials of Titanium in Various Electrolytes

The purpose of these experiments was to determine the single electrode potentials of titanium in various electrolytes and to study the effect of surface preparation and of immersion time on these values. The titanium metal specimens were 4 inches long, 0.75 inch wide, and 0.05 inch thick and the measurements were made with 2 inches of their length immersed in electrolyte at approximately 30° C. contained in open 250 milliliter beakers. Fresh electrolyte was used for each sample. All samples were washed with carbon tetrachloride and polished with 3/0 metallographic paper prior to immersion. Some samples were also aged at 130° C. or at room temperature for about 3 hours after polishing.

A summary of the initial and final electrode potentials and the times required to reach the final potentials is given in Table 2. Table 2A is a more complete summary, with enough intermediate values to indicate the shape of the time-potential curves. Typical curves are given in Figure 4.

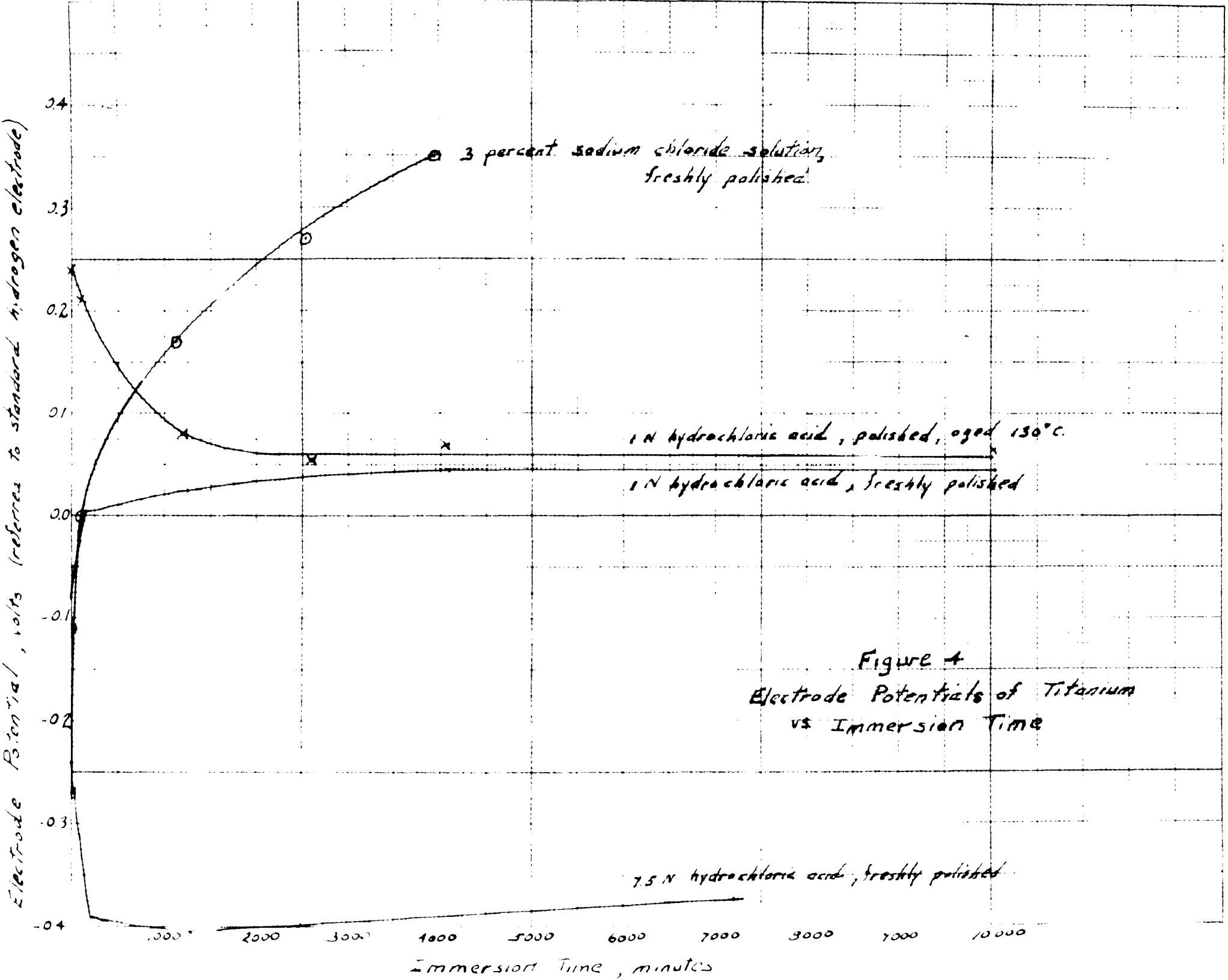

Figure 4
Electrode Potentials of Titanium
vs Immersion Time

Table 2 - Summary of Single Electrode Potentials of Titanium in Various Electrolytes at Room Temperature (referred to standard hydrogen electrode)

Electrolyte	Single Electrode Potential			
	Freshly polished	Polished, aged, 130° C. 3 hours	Polished, aged R. T. 3 hours	Annealed in vacuum 900° C. 2 hours, not polished
1% NaCl				
Initial	-0.31			
Final	0.34			
Time, minutes	18578			
3% NaCl				
Initial	-0.27	-0.01	-0.10	-0.11
Final	0.35	0.36	0.35	0.42
Time, minutes	3940	4127	4139	4277
N HCl				
Initial	-0.08	0.24	0.08	
Final	0.04	+0.07	0.06	
Time, minutes	4097	4047	2633	
7.5 N HCl				
Initial	-0.24	-0.01	0.28	
Final	-0.37	-0.37	-0.38	
Time, minutes	7345	133	1247	
6% SO_2 solution				
Initial	0.03	0.24	0.20	
Final	0.13	0.15	0.13	
Time, minutes	5779	5744	66	
1.1 N H_2SO_4 [a]				
Initial	-0.08	0.36	0.15	-0.12
Final	0.20	0.07	0.11	0.18
Time, minutes	1225	1364	1407	1131
2.2 N H_2SO_4				
Initial	-0.05	0.29	0.13	
Final	-0.33	-0.32	-0.34	
Time, minutes	72	156	82	

[a] See Table 2A for intermediate, high and low points.

Table 2A - Single Electrode Potentials of Titanium in Various Electrolytes at Room Temperature (referred to standard hydrogen electrode)

Electrolyte	Freshly polished		Polished, aged 3 hrs. 130° C.		Polished, aged 3 hrs. R. T.	
	Immersion time, minutes	Potential, volts	Immersion time, minutes	Potential, volts	Immersion time, minutes	Potential, volts
1% NaCl						
Sample 1	1.2	-0.23				
	6.1	-0.11				
	12.2	-0.04				
	93.1	-0.01				
	149.	0.00				
	356	0.07				
	2858	0.29				
	10058	0.32				
	18578	0.34				
Sample 2	0.5	-0.31				
	9936	0.33				
	18456	0.34				
3% NaCl	0.9	-0.27	1.2	-0.01	1.5	-0.10
	20	-0.11	35	0.10	19	-0.04
	130	0.01	191	0.24	197	0.05
	1135	0.17	1197	0.30	1202	0.19
	3940	0.35	4127	0.36	4139	0.35
	Annealed in vacuum 2 hrs. 900° C., not polished					
	3.0	-0.11				
	22	0.13				
	428	0.39				
	4277	0.42				
N HCl	1.1	-0.08	2.0	0.24	0.6	0.08
	123	-0.01	117	0.21	133	0.06
	1262	0.02	1197	0.07	1223	0.05
	2672	0.03	2607	0.06	2633	0.06
	4112	0.05	4047	0.07	4063	0.08
	10067	0.04	10017	0.07	10033	0.06
7.5 N HCl	1.2	-0.24	1.0	-0.01	0.7	0.28
	220	-0.39	132	-0.37	12	0.09
	1310	-0.41	1223	-0.38	38	-0.32
	7345	-0.37	7258	-0.37	1247	-0.38
	7400 [a]	-0.37	7273 [a]	-0.37	7282	-0.36
					7297 [a]	-0.37
6% SO_2 Solution	0.6	0.03	0.5	0.24	1.0	0.20
	4.1	0.05	1.8	0.23	65	0.13
	74	0.08	39	0.21	4771	0.13
	5779	0.13	5744	0.15		
1.1 N H_2SO_4	2.8	-0.09	1.2	0.36	0.8	0.15
	47	-0.29	44	0.26	59	-0.04
	90	-0.31	1179	0.02	82	-0.26
	1245	0.21	1364	0.07	1222	0.19
	1411	0.19			1407	0.11
	Annealed in vacuum 2 hrs. 900° C., not polished					
	1.1	-0.12				
	19	0.23				
	2580	0.18				
	3940	0.17				
2.2 N H_2SO_4	0.5	-0.05	1.2	0.29	1.5	0.13
	15.1	-0.28	23	0.27	32	0.05
	72	-0.33	101	0.00	110	-0.34
	183	-0.33	161	-0.31	164	-0.32
	4203	0.09	4180	0.08	4186	0.06
	5733 [b]	-0.29	5712 [b]	-0.30	5718 [b]	-0.32

[a] Put sample in fresh electrolyte just before measurement.

[b] Put sample in fresh electrolyte 25 hours before measurement.

These data show that when titanium is immersed in an electrolyte exposed to the atmosphere the single electrode potential of the metal usually changes very rapidly for a short time, then more slowly for a longer period of time, and finally reaches a fairly constant value. This steady-state value, which in these experiments was attained in from 66 to 4000 minutes, varies with the electrolyte but is approximately the same for various initial conditions of the titanium surface. The following values were obtained for the single electrode potentials of titanium: 3 percent sodium chloride 0.35 volt, 1.1 N sulfuric acid 0.2 volt, 6 percent sulfur dioxide in aqueous solution 0.13 volt, N hydrochloric acid 0.05 volt, 2.2 N sulfuric acid -0.33 volt, and 7.5 N hydrochloric acid -0.37 volt.

The initial electrode potentials, measured within one or two minutes of immersion, varied with both the electrolyte and the initial condition of the metal surface. Aged surfaces were always more electropositive than freshly polished surfaces in any particular solution. Aging at 130° C. generally made the metal more electropositive than aging at room temperature. Of the electrolytes used, only 7.5 N hydrochloric acid and 2.2 N sulfuric acid gave initial potentials for freshly polished titanium surfaces that were more electropositive than the final values. These were also the only solutions in which there was visible corrosion of the titanium specimens. With the exception of the specimens in sodium chloride solutions and the annealed specimen in 1.1 N sulfuric acid, all aged surfaces had initial electrode potentials that were more electropositive than the final potentials.

These results are reasonable when considered in the light of electrode potential theory summarized in the introduction. Specimens of titanium that have been aged in air have a more perfect film than freshly polished specimens and hence have a more electropositive initial potential. When the film is being repaired in an electrolyte the electrode potential becomes more electropositive and when it is being destroyed it becomes more electronegative. Various electrolytes have different capacities for film repair and, therefore, the steady-state potentials of titanium in different electrolytes are different. The condition of the titanium surface when immersed affects the initial potential but not the steady-state value.

The film repairing capacity of sodium chloride solution is so good that upon immersion even a specimen of titanium aged in air at 130° C. appears to acquire additional film and become more electropositive. But strong hydrochloric and sulfuric acid solutions destroy films and, therefore, the steady-state potentials are quite electronegative and the specimens corrode. Weaker sulfuric acid solution appears to destroy the film acquired in air and to form a new one in a relatively short time.

The data obtained in these experiments are in agreement with available information on titanium. The electrode potential of titanium in sea water as reported by Hutchinson and Perman[37] (+0.1 volt) is quite different from those obtained in the present study, but experimental conditions were also

different. The known resistance of titanium to sea water agrees with the data and observations summarized here. The resistance of titanium to weak solutions of acid and its lack of resistance to strong solutions of acid as noted here is also supported by the data of other investigators.

Single Electrode Potentials of a Few Common Metals in Three Percent Sodium Chloride and in 1.1 N Sulfuric Acid

As an aid in planning galvanic couple tests, the single electrode potentials of some of the common metals in 3 percent sodium chloride and in 1.1 N sulfuric acid exposed to the atmosphere were determined and the effects of surface preparation and immersion time on the potentials were studied.

The data summarized in Tables 3 and 4 reveal no important differences between the final electrode potentials of polished and unpolished specimens of any of the metals in either of the solutions. Furthermore, there were only small differences between the initial potentials of the polished and unpolished samples of all metals except aluminum, and there was relatively little change in electrode potential with time for all metals except for polished aluminum in sodium chloride and in sulfuric acid and stainless steel in sulfuric acid. The data for sodium chloride solution are in good agreement with the values presented by LaQue and Cox[41] for the electrode potentials of the various metals in similar solutions.

Table 3 - Single Electrode Potentials of Metals in 3% Sodium Chloride Solution

(referred to standard hydrogen electrode)

Metal	Initial		Final	
	Immersion time, minutes	Potential, volts	Immersion time, minutes	Potential, volts
Magnesium, degreased	2.0	-1.35	163	-1.34
Magnesium, degreased and polished	2.0	-1.43	163	-1.34
Zinc, degreased	0.8	-0.80	4069	-0.82
Zinc, degreased and polished	0.45	-0.81	4061	-0.81
Aluminum, degreased	0.9	-0.58	9959	-0.58
Aluminum, degreased and polished	0.7	-0.85	1075 9958	-0.52 -0.57
Black iron, scale pickled off, polished	1.4	-0.37	4278	-0.40
Copper, degreased	0.45	0.06	4115	0.00
Copper, degreased and polished	0.80	0.03	4123	-0.02
Stainless steel (18-8), degreased	0.6	0.10	4302	0.09
Stainless steel (18-8), degreased and polished			4250	0.10

Table 4 - Single Electrode Potential of Metals in 1.1 N Sulfuric Acid Solution

(referred to standard hydrogen electrode)

Metal	Initial		Final	
	Immersion time, minutes	Potential, volts	Immersion time, minutes	Potential, volts
Magnesium, degreased	0.8	-1.30	4.4	-1.25
Magnesium, degreased and polished	0.6	-1.29		
Zinc, degreased	0.6	-0.68	2971	-0.78
Zinc, degreased and polished	0.4	-0.71	2957	-0.77
Aluminum, degreased	0.9	-0.36	4120 10030 [a]	-0.25 -0.26
Aluminum, degreased and polished	1.9	-0.58	4116 10016 [a]	-0.26 -0.27
Black iron, scale removed, polished	0.3	-0.29	7241	-0.25
Copper, degreased	0.45	0.26	4115	0.28
Copper, degreased and polished	0.80	0.26	4123	0.29
Stainless steel (18-8), degreased	1.5	-0.16	1083 9985[a]	0.37 0.55
Stainless steel (18-8), degreased and polished	0.7	-0.15	9999 [a]	0.57

[a] White coating on surface.

Galvanic Couples in Three Percent Sodium Chloride Solution

The corrosion of galvanic couples of titanium with aluminum, magnesium, iron, copper, and 18-8 stainless steel in 3 percent sodium chloride solution was studied under comparable conditions of rotation, relative areas, atmosphere, etc. Additional tests were carried out with aluminum and magnesium to study the effect of changes in relative areas, speed of rotation, and type of atmosphere.

The testing method was a modification of that suggested by Fraser[21] and his coworkers and developed by Wesley.[61] The equipment consisted of an open two liter beaker, a rotating head, and an aerator. The titanium metal specimens weighed approximately 12 grams and were 4 inches long, 1 inch wide, and 0.05 inch thick and, after being cut to size, were annealed in vacuum at 900° C. for 2 hours. The other metal specimens were 4 inches long, 1 inch wide, and varied in thickness from 0.008 inch for aluminum to 0.12 inch for iron. The approximate weights in grams were as follows: aluminum 0.7, magnesium 5.0, iron 59, zinc 15, copper 40, stainless steel 40.

Two identical samples of each of the two metals were fastened to the rotating head, one of each pair being coupled together through a calibrated resistance (approximately 0.6 ohms). The coupled strips were in parallel positions, 2.25 inches apart. With the exceptions indicated, each sample had 4 square inches of submerged surface.

The metals were washed with acetone or carbon tetrachloride and were used without polishing. The areas above and just below the solution lines were covered with glyptal paint or cellulose acetate solution. Special care was taken with the clips used to hold the samples and with the surrounding areas since excessive corrosion was likely to occur at those points. The samples were rotated at various speeds up to 150 R.P.M. (linear velocity 86 feet per minute) and the tests were carried out at room temperature (28-35° C.). One and one-half liters of fresh solution was used in each test. The gas used in the test was passed through the solution for about one hour before the samples were placed in the solution. During the course of the test a few voltage readings were taken across the calibrated resistance for use in estimating the size of the galvanic current. At the end of the tests magnesium samples were dipped briefly in a hot solution containing 30 percent CrO_3 and 1 percent $AgNO_3$ before being washed, dried, and weighed. The dip was not necessary for other metals.

In the data summarized in Tables 5, 6, and 7, the "corrected galvanic loss is calculated by subtracting the weight loss of the uncoupled strip from the weight loss of the coupled strip. The assumption that the rate of non-galvanic corrosion is the same for both pieces of metal, upon which this calculation is based, is only approximately correct. The backs of the specimens were generally not insulated and it is assumed that both sides of each specimen undergo the same amount of corrosion. Actually, the side closer to the titanium

Table 5 - Galvanic Couple Tests, Titanium and Other Metals in 3% NaCl Solution, Air

Second metal	Electrode potential,[a] volts	Elapsed time, hrs.	Linear velocity of sample ft./min.	Loss in weight of aluminum, grams		Corrected galvanic loss, gm./hr.	Estimated galvanic current ma	Actual wt. loss / Theor. wt. loss
				Coupled	Uncoupled			
Zn	-0.80	21.4	75	0.4418	0.1653	0.013	1.6	6.5
Mg[b]	-1.35	22.6	75	0.4191	0.1731	0.011	11.4	2.3
Al	-0.58	17.4	75	0.0439	0.0005	0.0025	2.1	3.8
Fe	-0.39	41.5	69	0.3676	0.3195	0.0012	0.9	1.3
Cu	0.06	90.6	23	0.1036	0.0771	0.00029	0.06	2.5
Stainless steel	0.10	118.9	69	0.0007	0.0006	0.0000	0.0	-

[a] Values taken from Table 3.

[b] Average of 5 tests from Table 7, 75 feet per minute, air.

Table 6 - Galvanic Couple Tests, Ti-Al, in 3% NaCl Solution

Elapsed time, hrs.	Linear velocity of sample, ft./min.	Gas flowing through solution	Loss in weight of aluminum, grams		Corrected galvanic loss gm./hr.	Estimated galvanic current, ma	Actual weight loss / Theoretical weight loss
			Coupled	Uncoupled			
20.2	none	He	0.0058	0.0003	0.00027	0.3	2.8
23.2	none	He	0.0069	0.0018	0.0002	0.4	1.5
22.3	none	He	0.0098	0.0051	0.00021	0.4	1.6
20.0	none	He	0.0063	0.0000	0.0003	0.2	4.1
22.2	none	He	0.0017	0.0003	0.00006	0.15	1.6
18.7	none	air	0.0245	0.0007	0.00127	2.3	1.6
20.3	none	air	0.0223	0.0010	0.00107	2.2	1.4
24.1	none	air	0.0259	0.0004	0.00106	1.6	2.0
25.1[a]	12	air	0.0196	0.0015	0.0007	1.5	1.4
19.0	38	air	0.0352	0.0050	0.0016	1.9	2.5
17.4	75	air	0.0439	0.0005	0.0025	2.1	3.8
20.4[b]	23	air	0.0225	0.0022	0.001	1.2	2.4
16.8[b]	20	air	0.0323	--	0.00186	3.1	1.8
19.8[b]	23	air	0.0323	--	0.00122	1.5	2.4
21.6	23	N_2	0.0545	0.0002	0.0025	1.2	6.1
19.9	23	He	0.0199	0.0002	0.001	1.2	2.6

[a] Before test all specimens aged 47 hrs. in 3% NaCl. Electrode potentials: Ti + 0.3 volt
Al - 0.5 volt

[b] Area of aluminum and ratio of aluminum to titanium areas were as follows:
20.4 hr. test area Al 2 sq. in.; ratio 0.5
16.8 hr. test area Al 1.25 sq. in.; ratio 0.16
19.8 hr. test area Al 6 sq. in.; ratio 1.5.

Table 7 - Galvanic Couple Tests, Ti-Mg, in 3% NaCl Solution, Linear Velocity 75 feet per minute

Elapsed time, hrs.	Gas flowing through solution	Loss in weight of aluminum, grams		Corrected galvanic loss, grams per hr.	Estimated galvanic current, ma	Actual weight loss / Theoretical weight loss
		Coupled	Uncoupled			
19.7	He	.5570	.1668	0.020	22	2.0
19.9	He	.4082	.2249	0.0090	11	1.8
20.3[a,b]	He	.4602	.0419	0.021	28	1.6
16.6[b]	air	.3853	.0888	0.018	18	2.1
23.7	air	.4446	.1752	0.012	8	3.1
22.7	air	.3730	.1650	0.009	7	2.9
20.3	air	.3732	.1251	0.012	11	2.5
24.3	air	.3821	.1216	0.011	14	1.7
21.9	air	.5230	.2785	0.011	17	1.5
20.2[a,b]	air	.6121	.1030	0.025	29	2.0

[a] Area of Mg 2 sq. in.; ratio of Mg to Ti areas 0.5.

[b] Rotation different from others. Linear velocities in feet per minute:
20.3 hr. test 81
16.6 hr. test 86
20.2 hr. test none

usually corrodes more. The "estimated galvanic current" and the "theoretical weight loss" must be considered rough approximations since they are based upon a voltage which appears to vary considerably in magnitude during most tests and of which only a few readings were taken.

There was no chemical or galvanic corrosion of titanium in any of the tests carried out in 3 percent sodium chloride solution. A minute increase in weight, generally only a few tenths of a milligram, and occasionally a faint brown discoloration at the solution line were the only detectable changes in the titanium specimens. The data summarized in Table 5 show that all other metals tested except stainless steel and aluminum corroded chemically in 3 percent sodium chloride solution and that all except stainless steel corroded galvanically when coupled with titanium. Aluminum was the only metal in the group which corroded galvanically but not chemically. Available electrode potential data indicate that the stainless steel was electronegative to the titanium during most of the experiment. The passivity of the stainless steel must, therefore, be credited with its resistance to galvanic corrosion. The difference of potential, estimated at 0.25 volts, may be too small to overcome the passivity or perhaps the metal will not corrode in this electrolyte even with much larger voltages. Zinc, magnesium, and aluminum tended to form pits and pinholes, copper corroded more evenly, and iron corroded chiefly at the edges.

In general, the rate of galvanic corrosion increased as the differences between the single electrode potentials of

titanium and the second metal in the couple increased. Zinc is an exception to this rule and it almost falls into its proper position if the correlation is made between difference of potential and galvanic current. The actual weight losses are always greater than the theoretical weight losses and in the case of zinc the difference is very large. Perhaps the galvanic corrosion increases chemical corrosion by exposing more surface and by causing particles of metal to fall from the specimen, and the nature of zinc may be such that galvanic corrosion has an unusually large effect on its chemical corrosion. These data make the use of galvanic current values in the estimation of corrosion resulting from the coupling of two metals seem questionable. The galvanic currents were always much smaller than those predicted from electrode potential differences and the resistance of the circuit (estimated at less than 4 ohms). Apparently, polarization effects account for more than 99 percent of the voltage drop.

The data for titanium-aluminum and titanium-magnesium couples summarized in Tables 6 and 7 show that while corrosion rate values obtained in tests carried out under similar conditions are usually in general agreement, wide variations sometimes occur. A number of duplicate tests are probably necessary as the basis for important conclusions. The aluminum in titanium-aluminum couples at rest corroded about 5 times as much when air was passed through the solution as it did when helium was used. But when the couples were in motion the gas used had no effect. The explanation may be that sufficient air is drawn in by the rotation of the specimens to overcome the effect of the inert gas and to depolarize the titanium cathode surfaces.

Nitrogen caused more corrosion than helium, probably because it contained some oxygen. Chemical corrosion of aluminum was not appreciably affected by the gas or by rotation because it took place chiefly at contact points above the solution lines. The effect of motion was not investigated for magnesium-titanium couples. The results of the single titanium-aluminum couple test in which the specimens were polished and aged were similar to those of other tests. Apparently, equilibrium conditions are reached quickly. The galvanic corrosion of aluminum with air bubbling through the solution increases with velocity of motion in the range studied. When the Al area:T_i area is changed by a factor of 10 the total weight loss changes by a relatively small amount, but the smaller ratio results in 10 times as much loss per unit area.

Attempts to insulate submerged titanium surfaces with glyptal or cellulose acetate solutions failed. Similar experiments with aluminum or magnesium were generally successful.

PASSIVITY OF TITANIUM IN HYDROCHLORIC ACID, ELECTRODE POTENTIAL MEASUREMENTS

General Method

Although metals are seldom known to be passive in solutions of chloride ions,[45,59] available information indicated that titanium is quite resistant to fairly concentrated solutions of hydrochloric acid or sodium chloride. For this reason it was decided to study passivity of titanium in hydrochloric acid solutions.

Electrode potential measurements were made in order to observe the progress of passivation or "activation" without interrupting the experiment. All of these tests were made at room temperature (20°-28° C.).

C.P. chemicals and distilled water were used in preparing solutions and the hydrochloric acid and water were heated to boiling and stored in sealed bottles. Metal ions were added to the acid solutions in the form of standard chloride solutions. Solutions were generally made up in large batches to insure uniformity. The helium gas was 99.97 percent pure. The titanium metal used in these tests was prepared in Bureau of Mines laboratories from powder containing the following impurities: iron 0.1 percent, magnesium 0.35 percent, silicon 0.01 percent, manganese 0.02 percent, chlorine 0.1 percent, and nitrogen 0.02 percent. A sample of the final metal contained 0.13 percent iron, 0.064 percent magnesium, and 0.093 percent chlorine.

The specimens were 6.5 inches long, 0.25 inch wide, and approximately 0.05 inch thick. After the specimen was cut to size and the edges were rounded, it was annealed in vacuum at 900° C. for 2 hours.

The electrode potential measurements were made with a saturated calomel electrode and a type of K potentiometer using a saturated KCl salt bridge. The metal specimen was in a stoppered bottle 5 inches high and 1.875 inches in diameter. The rubber stopper had openings for gas inlet and outlet, potassium chloride bridge connection, and one or two titanium samples. The bottle contained approximately 3.5 inches of solution (160 ml.) and about 3 inches of the length of the sample was in contact with the solution. The titanium specimen was protected at the solution lines by enclosing it in wax filled glass tubes which passed through the stopper and extended to a point below the solution line, forming gas tight seals and permitting external electrical connections without solution line effects. Gas flow was measured with rotameters. The helium gas was passed through one or two water bottles before going to the specimen bottle while the air was first passed through three percent sodium hydroxide solution, two water bottles, and an empty bottle. When working with solutions of hydrochloric acid more concentrated than 5 N the gases were also passed through a sufficient number of hydrochloric acid bottles of such concentrations as to prevent depletion of the hydrochloric acid content of the specimen bottle. This precaution was found to be unnecessary when using solutions less than 5 N. Fritted glass gas dispersal tubes were used in many instances.

A fresh piece of titanium and fresh solution was used in each experiment. Gas was always passed through the solution for about 1 hour before bringing the titanium into contact with it and continuously throughout the experiment. The rate of flow was approximately 500 milliliters per minute for air and 100 milliliters per minute for helium. Just prior to immersion the titanium strip was washed with CCl_4, carefully polished with No. 1 metallographic paper, and placed in the sleeve. The first potentiometer reading was obtained as soon as possible after immersion and then at intervals determined by the rate of change of the electrode potential. The experiment was continued until the electrode potential reached a steady-state or longer and, of course, the specimen was not removed from the solution during the experiment. All of the initial and many of the final hydrochloric acid concentrations were determined by titration with standard sodium hydroxide.

Effect of Air

The objective of these experiments was to study the effect of air on the passivity of titanium by determining the electrode potentials of titanium in various concentrations of hydrochloric acid in contact with air or helium.

The initial, final, and enough of the intermediate electrode potential values to indicate the manner in which electrode potential changes with time are summarized in Table 8 and the steady state electrode potential values for titanium in helium and in air are plotted against hydrochloric acid concentrations in Figure 5. The change of potential with time for each set of conditions corresponds to the analysis of Evans[17]

Table 8 Electrode Potentials of Titanium in Hydrochloric Acid (referred to standard hydrogen electrode)

Normality of HCl	Helium		Air		Description of titanium specimen at end
	Immersion time, min.	Electrode potential, volts	Immersion time, min.	Electrode potential, volts	
Helium	2.5	-0.02	2.7	0.02	He - dull, corroded
1.00-1.02	111	-0.13	108	-0.02	
Air	465	-0.25	1434	0.02	Air - bright
1.00-0.99	1553	-0.30	6959	0.06	
	2578	-0.31	9605	0.07	
	1501	-0.27	14676	0.04	
	2568	-0.29	16181	0.05	
Helium	3.0	-0.01	1.3	0.04	He - dull, corroded
2.02-1.96	39.0	-0.10	425	-0.03	
Air	912	-0.33	2010	0.02	Air - bright
2.02-1.96	1234	-0.34	2987	0.03	
Helium	1.5	0.02	1.0	0.02	He - dull, corroded
2.97-2.90	24.6	-0.21	200	-0.20	
Air	43.9	-0.24	1452	-0.00	Air - uncorroded, but slightly dull
2.94-2.85	358	-0.33	1845	-0.14	
	1438	-0.34	3120	0.06	
			4350	0.06	
Helium	4.7	-0.06	7.2	0.06	He and air - dull, corroded
4.21-4.22	127	-0.31	141	-0.27	
Air	1170	-0.36	2697	-0.27	No visible evolution of gas
4.21-4.06					
Helium	2.0	0.00	1.6	0.01	He and Air - dull, corroded
4.95-4.91	199	-0.35	273	-0.31	
Air	1786	-0.37	2576	-0.27	A few bubbles visible at first, none later
4.95-4.69					
Air			1.3	0.04	Air - dull, corroded
7.06-7.34			36	-0.36	
			721	-0.36	
Helium	1.0	-0.22	3	-0.26	He and Air - dull, corroded
8.50-8.60	63	-0.37	30	-0.37	
Air	765	-0.39	1006	-0.38	A few gas bubbles visible at first, none later.
8.50-8.55	1390	-0.39			Solution faint purple
Helium	1.3	0.09	2.0	-0.38	He and Air - dull, corroded
10.0-10.3	13	-0.38	16.3	-0.40	
Air	269	-0.39	1718	-0.36	Visible gas evolution
10.0-10.7	2323	-0.38	1727 [a]	-0.39	Solution He faint purple, air purple

[a] After replacing the solution which contained titanium ions with fresh electrolyte through which air had been passed for 45 minutes.

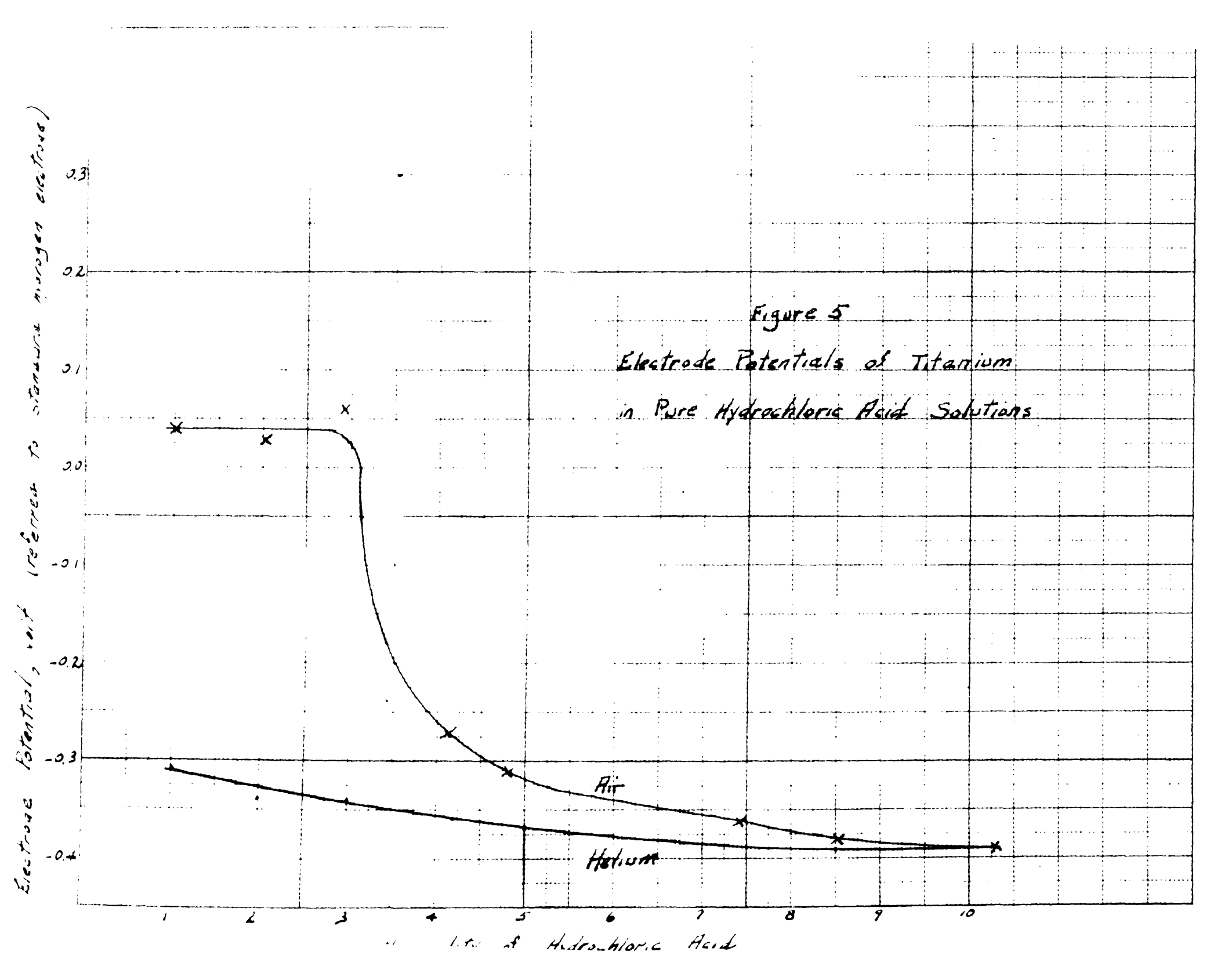
Figure 5
Electrode Potentials of Titanium
in Pure Hydrochloric Acid Solutions
Electrode Potential, volts (referred to standard hydrogen electrode)
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
Air
Helium
1
2
3
4
5
6
7
8
9
10
Hydrochloric Acid

mentioned earlier. When the metal is becoming passive, presumably by building up an oxide film, the electrode potential becomes more positive. Destruction of the film and increasing tendency to corrode is indicated by change in the electronegative direction. The rapidity with which the steady state value is reached varies widely. In the 3 N hydrochloric acid with air atmosphere, which appears to be a borderline condition between passivity and activity, the electrode potential rises and falls before it reaches a steady-state. In 1 and 2 N hydrochloric acid with air atmosphere the condition of passivity is reached more quickly. In all experiments with helium atmospheres the steady state was reached quite rapidly and the time required to reach it decreased with increasing acid concentration; the time was only 13 minutes in 10 N acid.

In a helium atmosphere, the electrode potential of titanium is between -0.3 and -0.4 volts in all acid concentrations between 1 and 10 N. The electrode potentials in air are generally more electropositive than in helium but the differences are much greater in concentrations less than 4 N. In air the potential becomes more electronegative very markedly between 3 and 4 N. In no instance is the electrode potential more electronegative than -0.4 volts. This does not agree with the calculated value of Latimer[40] (1.75 volts). However, it is not too different from the value of Botts and Krauskopf[2]. These investigators present a value of -0.23 volt for the single electrode potential of titanium in M/4 solution of $TiCl_3$ but had difficulty in reproducing results probably because of variations in the condition of the metal surface.

The titanium metal appears to corrode appreciably at electrode potentials more electronegative than -0.27 volt. These could be called corrosion potentials. Corrosion of sufficient intensity to dull the surface of the metal takes place in all concentrations of acid from 1 to 10 N in helium atmospheres and in all concentrations over 3 N in air atmospheres. There was no pitting. This is in general agreement with existing corrosion data for air atmospheres; data for the corrosion of titanium in helium atmospheres are not available in the literature. The data presented here also agree with the general belief that titanium is more stable in oxidizing atmospheres.

In some of the experiments temporary changes were made in the rate of gas flow to study the effect of air supply. In 8.5 N acid the flow of helium was raised to 500 millliliters per minute and then lowered to 20 millliliters per minute without changing the electrode potential; raising the flow to 600 millliliters per minute in 1, 2, 3, and 4 N acid also failed to change the potential in 10 or 20 minutes. But with air atmospheres in 7 N acid the following data were obtained within a 15 minute period: 550 ml. -0.36 volt, 130 ml. -0.37 volt, 35 ml. -0.39 volt, 700 ml. -0.36 volt, 500 ml. -0.36 volt.

The data summarized in Table 8 are in general agreement with an earlier series of experiments carried out in a somewhat different manner. The same titanium specimens were used to determine the electrode potentials in both atmospheres for any particular acid concentration, first helium and then air being passed through the specimen bottle. These early data

were discarded but they do indicate that a corroding surface can sometimes be passivated by contact with air. For example, in 1 N hydrochloric acid the potential of a piece of titanium at -0.25 volt in helium rose to -0.07 5 minutes after the flow of air began and to +0.03 in 216 minutes.

Exploratory Experiments on the Effect of Dissolved Metals

Electrode potential measurements of titanium metal in aerated and non-aerated solutions of hydrochloric acid made during galvanic couple experiments indicated that the presence of dissolved copper causes titanium to become much more electropositive (noble) than it is in pure hydrochloric acid solutions without visible deposition of copper or any change in the original appearance of the titanium metal. This observation was verified by means of potential measurements made in the usual way. Although cuprous chloride was used in preparing the standard copper solution from which the experimental solutions were made up most, if not all, of the copper was oxidized to the cupric state before the beginning of the experiments.

In one experiment the potential of a strip of titanium was -0.21 volt 174 minutes after immersion in pure 0.96 N HCl in helium atmosphere. At 176 minutes copper was added to the solution to a concentration of 4 milligrams per liter and at 181 minutes after immersion the potential was 0.19 volt; at 212 minutes it was 0.37 volt. In another experiment the electrode potential of a piece of titanium reached -0.32 volt 168 minutes after immersion in pure 4.97 N HCl with air atmosphere. At 170 minutes the solution was given a copper

concentration of 1300 milligrams of copper per liter and at 171 minutes the potential was 0.49 volt, at 1219 minutes 0.69 volt, at 4454 minutes 0.69 volt. At the end of the experiment the titanium showed signs of slight corrosion which undoubtedly occurred before the copper was added. There was no visible deposit of copper on the titanium specimen or in the vessel. A series of experiments was carried out to study the effect of copper ions on titanium with various surface preparations. The solution was hydrochloric acid approximately 1 N in concentration with 9 milligrams of copper per liter and the work was done in open beakers with a flow of 500 milliliters of air per minute. The electrode potential values summarized below are for 30 minutes of immersion, except where other times are given:

1) unpolished titanium 0.28 volt in pure acid and 0.58 in acid containing copper.
2) polished titanium 0.05 volt in pure acid and 0.27 volt in copper solution.
3) samples polished and dipped in pure 5 or 10 N HCl for 5 or 10 minutes before immersion in copper solution 0.30 volt.
4) unpolished titanium heated at 155° C. for 20 hours 0.58 volt 37 minutes after immersion and 0.52 volt at 1260 minutes.
5) polished titanium aged for 3 hours at room temperature 0.32 volt at 20 minutes and 0.40 at 1217 minutes after immersion in copper bearing solution.

6) polished titanium aged at 155° C. for 3 or 20 hours 0.53 to 0.54 volt at 25 minutes and 0.50 to 0.52 volt at 1200 minutes after immersion in copper bearing solution.

These data indicate that small concentrations of dissolved copper make the electrode potential of both polished and unpolished titanium much more electropositive without visible precipitation of copper. Pretreatment of polished titanium with strong hydrochloric acid slightly increases the passivating effect of the copper ion. The electrode potential of titanium polished and aged in air before immersion in copper bearing solution approaches that of unpolished metal in the same electrolyte. The results of other experiments indicate that the high potential acquired by titanium immersed in solution containing copper ions is virtually gone after 30 minutes contact with pure acid.

Other experiments carried out in the same manner with 1 N HCl, air atmosphere and higher copper concentrations resulted in the following electrode potential values:

1) 200 milligrams copper per liter 0.55 volt for polished titanium and 0.66 volt for unpolished titanium after 35 minutes of immersion.

2) 2000 milligrams copper per liter 0.66 volt for polished titanium and 0.67 volt for unpolished titanium after 30 minutes of immersion.

These data show that increasing the copper concentration from 9 milligrams to 200 milligrams per liter greatly increases the passivity of titanium after 30 minutes immersion and that raising

the copper concentration to 2000 milligrams has an additional effect. Higher copper concentrations have relatively little effect on the electrode potential of unpolished titanium. These conclusions may not be correct for longer immersion times. There is no visible precipitation of copper no matter how high the copper ion concentration.

Electrode potential measurements made in air atmospheres with 1 N hydrochloric acid containing 200 milligrams of cobalt or zinc per liter indicated that these metals also made titanium passive without visible deposition. The following electrode potentials are for 30 minute immersion times: (1) 200 milligrams cobalt per liter 0.44 volt for polished and 0.57 volt for unpolished titanium (2) 200 milligrams zinc per liter 0.16 volt for polished and 0.43 volt for unpolished titanium.

Effects of Various Dissolved Metals

Experiments were carried out to study the effect of various dissolved metals on the passivity of titanium metal in 1 N hydrochloric acid and helium or air atmospheres. Metals were chosen for a variety of single electrode potentials, overvoltages, and other characteristics. The copper used in these experiments appeared to be in the cupric state. In the experiments with iron, the total iron content of the solution was 181 milligrams per liter and the ferrous iron content was 178 milligrams per liter when it was placed in the specimen bottles. In the helium experiment the iron undoubtedly remained in the ferrous state throughout the experiment but in the air experiment

the iron was probably oxidized before immersion of the specimen. Certain specimens were not polished, as indicated in Table 11.

The initial, final, and a few of the intermediate electrode potentials are summarized in Tables 9, 10, and 11. In every case the presence of the metal ion causes the metal specimen to acquire a more electropositive electrode potential. In general, the steady state is reached quickly. It may be concluded that the metal ions passivate titanium and decrease its tendency to corrode. The appearance of the polished titanium specimens immersed in 1 N hydrochloric acid solutions in helium atmospheres confirms this conclusion. In pure solutions the specimens acquired a corroded appearance while in all other experiments of this series the specimens remained bright and shiny. None of the specimens corroded in air atmospheres and unpolished specimens did not corrode in either helium or air. There was no visible deposit of any kind either on the titanium specimen or in the solution in any of the experiments summarized in Tables 9, 10, and 11.

The magnitude of the effect of the metal ions on the electrode potentials of the specimens, and presumably on their passivity, is apparently related to the electropositiveness of their single electrode potentials. When this generalization seems to fail one may assume that the reaction involved at the surface of the specimen is not between the metal and its ion. For example, iron with a single electrode potential of -0.44 volt has an effect between that of platinum and mercury. But the pertinent reaction is probably $Fe^{++} = Fe^{+++} + e$ $E^{o} = 0.75$ volt.

Table 9 - Electrode Potential of Titanium in 1 N HCl containing 0.003 mole of Dissolved Metals per liter, Helium Atmosphere, Titanium Polished

Dissolved metal	Electrode Potentials, volts: Initial Time, min.	Initial Pot.	Peak of initial rise Time, min.	Peak of initial rise Pot.	Intermediate readings Time, min.	Intermediate readings Pot.	Intermediate readings Time, min.	Intermediate readings Pot.	Final Time, min.	Final Pot.	Remarks
Au	1.3	0.87	31	0.90	332	0.90			1444	0.90	
Cu	3.2	0.49	16	0.56	46	0.58			164	0.58	
Pt	3.0	0.39	22	0.45	160	0.47	1567	0.47	3033	0.48	No visible deposition of any kind. No change in appearance of titanium surface or solution
Fe	3	0.16	30	0.25	1024	0.33	1329	0.33	2689	0.30	
Hg	4	0.30	9	0.30	58	0.29	1485	0.29	2855	0.29	
Zn	4	-0.17	226	-0.05	1097	0.07	1400	0.11	1544	0.12	
Co	1.8	-0.08	198	-0.12	1284	0.01	1764	0.03	7314	0.12	
Al	5.0	-0.14	45	-0.11	136	-0.09			1467	0.04	
Mg	12	-0.10	38	-0.05	106	-0.05	1203	-0.05	2704	0.04	
None	4	-0.21	30	-0.16	122	-0.16	1501	-0.27	2568	-0.29	Surface of titanium specimens, dull and corroded
None	2	-0.02	111	-0.13	465	-0.25	1553	-0.30	2578	-0.31	

Table 10 - Electrode Potential of Titanium in 1 N HCl containing 0.003 mole of Dissolved Metals per liter, Air Atmosphere, Titanium Polished

Dissolved metal	Electrode Potentials, volts										Remarks
	Initial		Peak of initial rise		Intermediate readings				Final		
	Time, min.	Pot.	Time, min.	Pot.	Time, min.	Pot.	Time, min.	Pot.	Time, min.	Pot.	
Au	1	0.82	7	0.87	289	0.90	1378	0.91	2699	0.91	
Cu	4	0.48	36	0.56	93	0.57	1358	0.59	2455	0.58	
Pt	2	0.39	26	0.46	59	0.47	1573	0.48	4487	0.48	No visible deposit of any kind. No change in appearance of titanium surface or solution
Fe	3	0.17	60	0.31	1069	0.39	1374	0.40	2794	0.42	
Hg	17	0.29							4171	0.30	
Zn	1	-0.09	157	0.06	996	0.22	1175	0.30	1235	0.30	
Co	1	-0.12	32	0.05	181	0.17	1387	0.22	1476	0.23	
Al	2	0.06	14	0.04	442	0.05	1439	0.15	1525	0.15	
Mg	4	0.09	42	-0.02	173	0.01	1631	0.06	5671	0.16	
None	3	0.02			108	-0.02	1434	0.02	9605	0.07	
None	5	-0.07			156	0.02	216	0.03			

Table 11 - Electrode Potential of Titanium in 1 N HCl containing 0.003 mole of Dissolved Metals per liter, Air or Helium Atmosphere, Titanium Unpolished

Dissolved metal	Electrode Potentials, volts: Initial Time, min.	Initial Pot.	Peak of initial rise Time, min.	Peak of initial rise Pot.	Intermediate readings Time, min.	Intermediate readings Pot.	Intermediate readings Time, min.	Intermediate readings Pot.	Final Time, min.	Final Pot.	Remarks
					HELIUM ATMOSPHERE						
Au	1	0.81	9	0.90					1467	0.91	
Cu	4	0.06	32	0.60	111	0.61			113	0.60	
Zn	2	-0.21			167	0.06	1073	0.21	1521	0.23	No visible
Al	5	-0.14	29	0.15	82	0.26	118	0.26	1449	0.26	deposit of
None	9	-0.17	48	0.26	104	0.29	1300	0.07	2745	0.06	any kind
					AIR ATMOSPHERE						No change in
Au	1	0.81	35	0.85					2691	0.91	appearance of
Cu	4	0.58	19	0.64					2392	0.59	titanium sur-
Al	2	0.20	11	0.38					1520	0.33	face or solu-
None	3	-0.14	46	0.40	195	0.41	1015	0.33	2482	0.35	tion

In this way, the fact that iron differs from gold, copper, and platinum in that it has more passivating effect in air than it has in helium can be explained on the basis of more ferric ions. The importance of ferric ions was demonstrated by adding metallic iron to the vessels at the end of each experiment with iron. In air atmosphere the electrode potential dropped from 0.42 to 0.09 volt in 3 minutes and then increased again. However, in helium the electrode potential slowly became more electronegative as the few ferric ions were reduced and it remained so because the ferrous ions were not reoxidized. A number of hours later the electrode potential was -0.34 volt and the specimen was corroding. With zinc, cobalt, aluminum, and magnesium the reactions also seem to be different from those of the single electrode potentials. The effect of air in these cases may be explained by assuming that the ions contain oxygen. This explains the fact that a metal as electronegative as magnesium can passivate a titanium surface, in other words act as an oxidizing agent. If the action of these metals does involve compounds, acid concentration may have a large effect. The presence of air has no effect with gold, copper, platinum, and mercury.

There may or may not be thin, transparent deposits of metal or compound on the titanium surfaces. But the large changes in electrode potential indicate that a large portion of the metal surface is involved. The electrode potentials obtained with gold and mercury ions are less positive than the single electrode potentials of these metals. This is to be expected since the tendency to deposit (or act as an oxidizing agent) decreases

with concentration. The fact that copper results in an electrode potential more positive than its single electrode potential (0.34 volt) is more difficult to explain. Perhaps only the more electronegative of the titanium surfaces are involved.

Effect of Copper in Various Concentrations of Hydrochloric Acid

Experiments were carried out to study the effect of 200 milligrams of copper per liter on the passivity of titanium in various concentrations of hydrochloric acid up to 10 N in atmospheres of helium and air. Except where it is otherwise indicated, three acid concentrations were studied at one time with the gas flow in series. The following normalities were grouped together in the order given with empty bottles between sample bottles: 2, 3, 4; 5, 6, 7; 8, 9, 10. No provision was made for maintaining acid concentrations. Depletion was small for acid concentrations of 5 N or less but quite large for 8 to 10 N solutions. The experiments with 10 N acid were repeated with preliminary acid bottles to maintain the acid concentrations.

Significant, comparable data are summarized in Tables 12 and 13. In general, the electrode potentials became very electropositive quickly, rise modestly to a peak, and drop slowly. Plots of 1-5 minute immersion, peak, and 2700 minute potentials against normality are all quite flat (Figures 6 and 7), the most rapid changes taking place in the 1-5 minute plots between 1 and 5 N. The most electropositive potentials in both

Table 12 - Electrode Potentials of Titanium Specimens in HCl Solutions Containing 200 milligrams Copper (.003 mole) per liter, Helium Atmosphere

Normality of acid	Electrode Potentials, volts: Initial Time, min.	Initial Pot.	Peak Time, min.	Peak Pot.	Steady state Time, min.	Steady state Pot.	Time, min.	Time, Pot.	Final Time, min.	Final Pot.	Remarks
1[a]	3.2	+.49	47	+.58	164	+.58	2700				No visible corrosion
2	1.5	+.42	47	+.58	1284	+.58	2700	+.58	4104	+.58	" " "
3	1.0	+.56	34	+.64	1238	+.62	2700	+.63	4064	+.62	" " "
4	1.3	+.59	12	+.65	1366	+.63	2700	+.62	4198	+.62	" " "
5	1.0	+.57	12	+.66	1188	+.63	2700	+.62	7260	+.60	" " "
6	2.7	+.65	8	+.66	1410	+.64	2700	+.62	7197	+.58	" " "
7	3	+.65	34	+.66	1357	+.63	2700	+.62	7162	+.60	" " "
8	2	+.63	40	+.64	1417	+.59	2700	+.56	3117	+.54	No visible corrosion Corroded area under sleeve
9	1.5	+.61	32	+.63	1369	+.60	2700	+.60	3064	+.59	No visible corrosion, slight tarnish
10	1.7	+.60	32	+.61	1352	-.39	2700	-.39			Titanium corroding
10[a]	2	+.58	15	+.60	1300	+.58	2700		2365	+.58	No visible corrosion, slight tarnish
10[a,b]	2	+.57	12	+.59	1218	+.53	2700		2680	+.45	No visible corrosion, slight darkening. Slight corrosion under sleeve.

[a] Experiment carried out alone.
[b] Hydrochloric acid concentrations: Initial 10.05 N, Final 9.95 N

Table 13 - Electrode Potentials of Titanium Specimens in HCl Solutions Containing 200 milligrams Copper (.003 mole) per liter, Air Atmosphere

Normality of acid	Electrode Potentials, volts: Initial Time, min.	Initial Pot.	Peak Time, min.	Peak Pot.	Steady state Time, min.	Steady state Pot.	Final Time, min.	Final Pot.	Final Time, min.	Final Pot.	Remarks
1[a]	4	+.48	1358	+.59	1478	+.59	2700		2455	+.58	No visible corrosion
2	4	+.53	155	+.61	1168	+.58	2700	+.58	2756	+.58	" " "
3	2	+.57	24	+.62	1024	+.61	2700	+.61	2713	+.61	" " "
4	1	+.60	41	+.65	1088	+.64	2700	+.64	2680	+.64	" " "
5	4	+.64	368	+.68	1252	+.68	2700	+.66	4199	+.66	" " "
6	1.5	+.62	300	+.67	1135	+.66	2700	+.63	4097	+.63	" " "
7	1.2	+.62	241	+.67	1106	+.66	2700	+.65	4064	+.64	" " "
8	1.7	+.63	173	+.66	1685	+.64	2700	+.64	4510	+.49	No visible corrosion Slight corrosion under sleeve
9	1.8	+.61	140	+.65	1555	+.62	2700	+.62	4366	+.62	No visible corrosion Slight corrosion under sleeve
10	1.0	+.59	36	+.62	1473	+.60	2700	+.60	4288	+.55	No visible corrosion Slight corrosion under sleeve
10[a,b]	2	+.61	17	+.63	1203	+.51	2700		2698	+.40	No visible corrosion on immersed portion. Corrosion above soln. line

[a] Experiment carried out alone
[b] Hydrochloric acid concentration: Initial 10.05 N Final 9.45 N

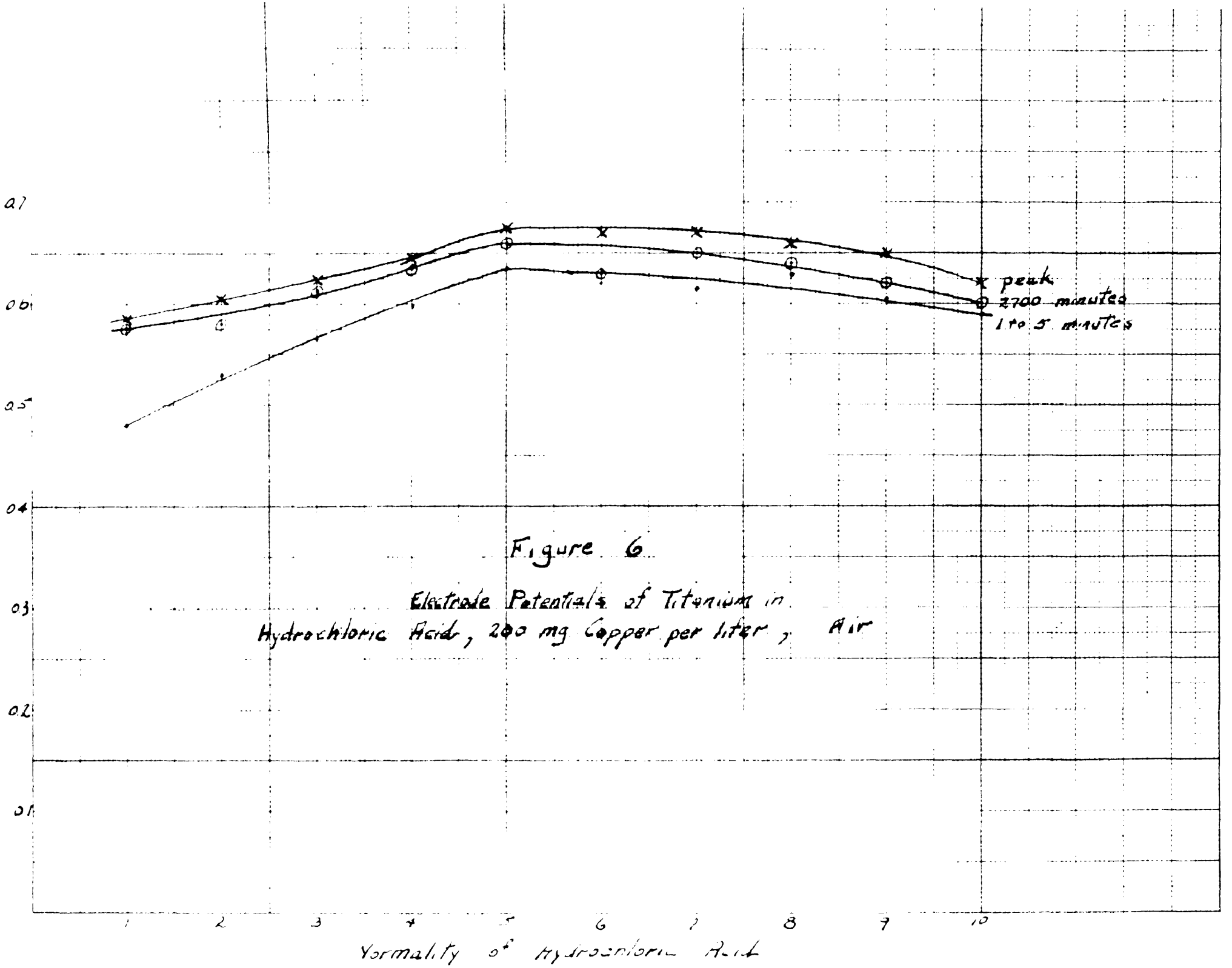

Figure 6

Electrode Potentials of Titanium in Hydrochloric Acid, 200 mg Copper per liter, Air

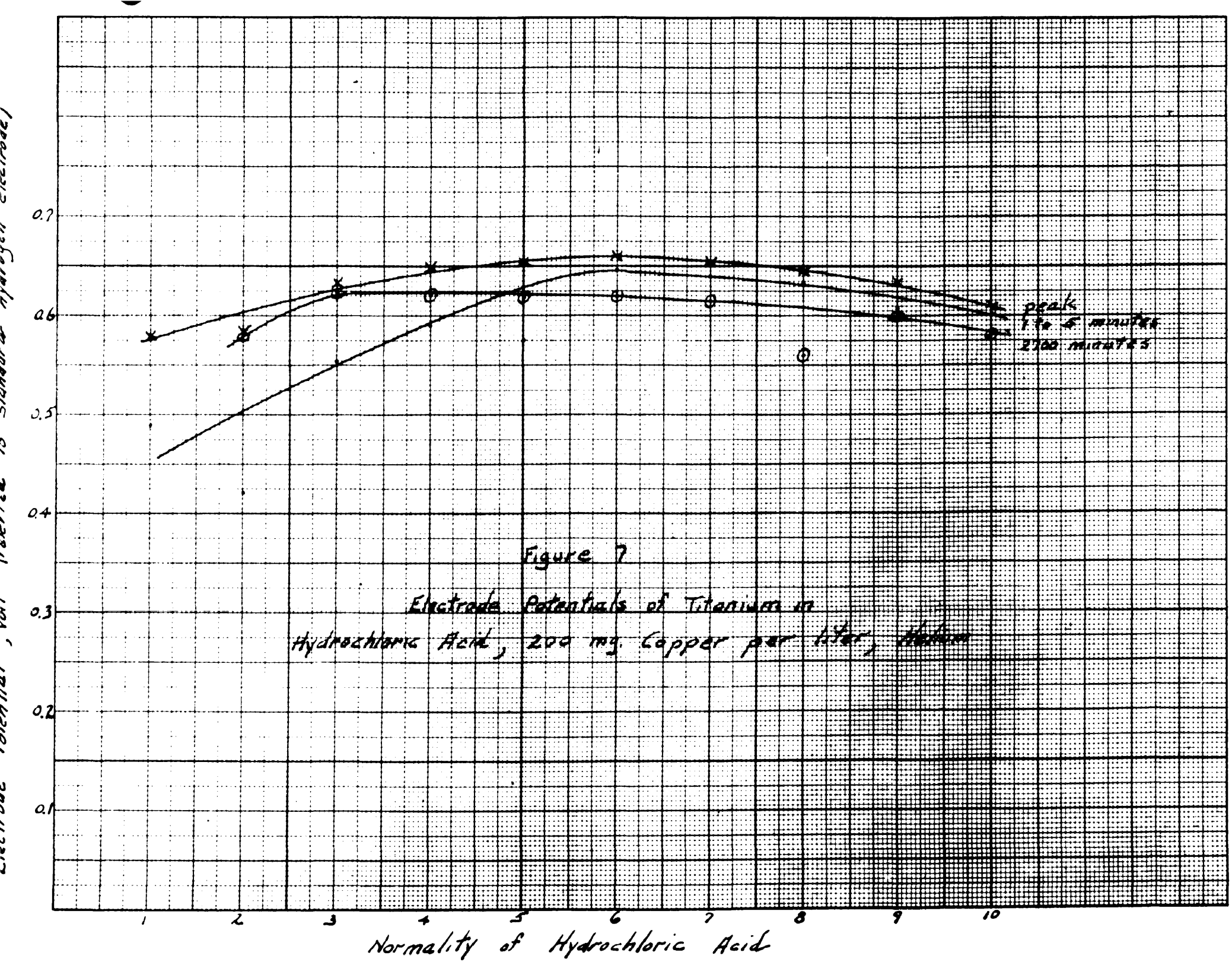

Figure 7

Electrode Potentials of Titanium in Hydrochloric Acid, 200 mg. Copper per liter, Medium

air and helium atmospheres occur at 5 to 7 N for all times mentioned. There was no indication of corrosion in any acid concentration less than 7 N in either atmosphere nor any indication that passivity was breaking down even after more than 3 days of immersion. The specimens were bright and shiny at the end of each experiment. But in 8, 9, and 10 N acid solutions there were indications of a breakdown in passivity. But with one exception, there was no corrosion of immersed titanium even after 2 or 3 days, only a fall in electrode potential and slight tarnish. This breakdown appears to start in sheltered areas, as for example under the sleeves. Here corrosion often occurred in 8 to 10 N acid solutions with both air and helium. Some of the drop in electrode potential of the specimens could be the result of these corroding areas. In the experiment with 10 N acid and helium atmosphere when the titanium corroded rapidly red copper powder precipitated but in no other instance was solid copper visible either on the specimen or in the solution.

A possible explanation for the higher electrode potential at 5 N acid is that up to this concentration the active areas of the metal are increasing and, therefore, more of the surface reacts with the copper.

Effect of Various Concentrations of Copper

The effects of copper concentrations of 0, 2, 20, and 200 milligrams per liter on the passivity of copper in 1, 5, and 10 N hydrochloric acid solutions were compared.

The data summarized in Tables 14, 15, and 16 indicate that 2 milligrams of copper per liter passivates titanium in 1 N acid, 20 milligrams are required in 5 N, and 200 milligrams are

Table 14 - Effect of Copper Concentration in 1 N HCl, He and Air

Copper conc., mg. per liter	Electrode Potentials, volts: Initial Time, min.	Initial Pot.	Peak Time, min.	Peak Pot.	Steady state Time, min.	Steady state Pot.	Final Time, min.	Final Pot.	Remarks
				HELIUM					
None	2	-0.02				1553	-0.30	2578	-0.31	Titanium dull and corroded
2	2.0	0.07	4300	0.44				8469	0.43	No visible corrosion
20	2.0	0.20	168	0.48	1443	0.48		7345	0.48	No visible corrosion
200	3.7	0.49	47	0.57				164	0.58	No visible corrosion
				AIR					
None	2.7	0.02				6959	0.06	16181	0.05	Titanium bright and shiny
2	1.3	0.06	5502	0.44				9932	0.43	No visible corrosion
20	1.5	0.19	4936	0.49				15930	0.45	No visible corrosion
200	1.7	0.48	1358	0.59	1478	1610	0.58	2455	0.58	No visible corrosion

Table 15 - Effect of Copper Concentration in 5N HCl, He and Air

Copper conc., mg. per liter	Electrode Potentials, volts										Remarks
	Initial		Peak		Steady state				Final		
	Time, min.	Pot.	Time, min.	Pot.	Time, min.	Pot.	Time, min.	Pot.	Time, min.	Pot.	
					HELIUM						
None	2	0.00							1786	-0.37	Titanium dull and corroded
2	1.8	-0.17	85	-0.34	1673	-0.35	4148	-0.36	7008	-0.38	Titanium corroded
20	2.6	0.42	75	0.58	1348	0.58			7278	0.55	No visible corrosion
200	1	0.57	12	0.66			1188	0.63	7260	0.60	No visible corrosion
200	2	0.62	28	0.64					71	0.64	No visible corrosion
					AIR						
None	1.6	0.01	273	-0.31					2576	-0.27	Titanium dull and corroded
20	3	0.54	500	0.59	1420	0.57	9255	0.56	16290	0.55	No visible corrosion Slight stain
200	4.3	0.64	368	0.68			1252	0.68	4199	0.65	No visible corrosion

Table 16 - Effect of Copper Concentration in 10 N HCl, He and Air

Copper conc., mg. per liter	Electrode Potentials, volts: Initial Time, min.	Initial Pot.	Peak Time, min.	Peak Pot.	Steady state Time, min.	Steady state Pot.	Steady state Time, min.	Steady state Pot.	Final Time, min.	Final Pot.	Remarks
					HELIUM						
None	1.3	0.05							2323	-0.38	Titanium corroded rapidly
20[a]	1.5	0.44	46	0.57	3927	0.35	5427	-0.40	7202	-0.40	Titanium corroded
200	2	0.57	12	0.59			1218	0.53	2680	0.45	No visible corrosion Slight tarnish
					AIR						
None	2.0	-0.38	16	-0.40					1727	-0.39	Titanium corroded rapidly
20[a]	2	0.52	1362	0.60					2577	0.57	No visible corrosion
200	2	0.61							2698	0.40	No visible corrosion on immersed portion; corrosion above soln. line

[a] The final acid concentrations were much less than 10 N.

required in 10 N. Smaller amounts of copper result in passivity for shorter periods. In 10 N acid passivity seems to be decreasing at the end of 2 days even with 200 milligrams of copper per liter.

Electron diffraction examination of the surface of the specimen immersed in 5 N acid, 200 mg. copper, helium atmosphere for 71 minutes with final electrode potential of 0.6[illegible] volt failed to show the presence of copper, copper oxide, copper chloride, titanium dioxide, titanium monoxide, or titanium nitride crystallites. One would, therefore, assume that if a layer of copper is present as such it is less than 10 to 100 A° thick. At the same time, none of the compounds mentioned above were detected in either of the following specimens:

1) titanium metal exposed to 1 N hydrochloric acid, air
2) freshly polished titanium.

PASSIVITY OF TITANIUM IN HYDROCHLORIC ACID, CORROSION TESTS

The effect of copper on the corrosion rate of titanium at room temperature in hydrochloric acid with helium and air atmospheres was studied. The titanium metal, chemicals, and helium, the preparation of solutions, the preliminary treatment of the gases, and the preparation of metal specimens were as described in the last section. However the specimens were smaller, 3.375 inches long, 0.25 inch wide, and 0.05 inch thick. The specimen bottles were 5.5 inches high, 3.5 inches in diameter, and had volumes of 600 milliliters. The shape of the bottle and its dimensions were such that one end of the specimen rested on the bottom of one side of the bottle while the other end rested about 1.5 inches up on the opposite side. Of course, the specimens were totally immersed.

Each test was started with a fresh metal specimen and 400 milliliters of fresh solution. Approximately 500 milliliters of air or 100 milliliters of helium per minute were passed through the solution for approximately one hour before immersion of the specimen and continuously throughout the test. With a few exceptions, the experiments were three days long. After removal from the solution the specimens were washed, dried and weighed.

The data summarized in Tables 17 and 18 are in good general agreement with conclusions based on electrode potential measurements. With a flow of air, titanium is resistant to pure

Table 17 - Effect of Copper on Corrosion of Titanium in HCl Solutions, Air Atmospheres

Normality of Acid		Time, days	Weight loss,[a] mg	Weight loss, milligrams per sq. in. per day				Appearance of specimen at end
Initial	Final			No Cu	2 mg Cu per liter	20 mg Cu per liter	200 mg Cu per liter	
1.00	0.99	3.01	0.2				.03	Bright, smooth, unchanged
1.00	1.00	3.23	0.0			none		" " "
1.00	1.00	3.10	0.2		.03			" " "
1.01	1.00	2.99	0.1	.02				" " "
3.0	2.87	3.00	0.4				.07	Bright, smooth, unchanged
2.94	2.91	3.23	0.0			none		" " "
3.0	3.03	3.10	0.2		.03			" " "
2.97	2.92	2.99	1.1	0.18				" " "
5	4.8	3.00	0.5				.08	Bright, smooth, unchanged
5.1	4.7	3.22	0.0			none		" " "
5	4.8	3.10	0.1		.02			" " "
5.0	4.8	2.98	22.6	3.77				Corroded
10.1	7.0	3.00	0.4				.07	Bright, smooth, unchanged
9.9	7.2	3.22	0.4			.06		" " "
10.3	6.7	3.10	125.2		20.8			Corroded
10	7.8	2.97	78.6	13.0				"
10.3	9.5	0.436	23.0		26.4			"
10.3	9.4	0.625	24.7	19.8				"
9.8	9.10	3.02	309.1	52				Corroded
9.8	9.22	3.00	284.4	48				"
9.8	9.2	3.01	352.5		60			"
9.8	9.1	3.01	283.1		48			"

[a] Original weight of specimen 2.9 to 3.2 grams.

Table 18 - Effect of Copper on Corrosion of Titanium in HCl Solution, Helium Atmosphere

Normality of Acid		Time, days	Weight loss,[a] mg	Weight loss, milligrams per sq. in. per day				Appearance of specimen at end
Initial	Final			No Cu	2 mg Cu per liter	20 mg Cu per liter	200 mg Cu per liter	
0.997	0.998	3.103	2.4	0.39				Dull
1.00	1.00	3.024	1.2	0.20				Slight dullness
1.00	-	3.078	0.0		0.0			Bright, smooth, unchanged
2.94	2.94	3.022	8.0	1.34				Corroded
2.97	2.93	3.072	7.8	1.27				Corroded
3.03	3.05	3.024	0.2		.03			Bright, smooth, unchanged
2.96	2.93	3.035	0.3			.05		Bright, smooth, unchanged
4.21	4.21	3.016	14.3	2.4				Corroded
4.95	5.00	3.010	17.2	2.9				Corroded
5.12	5.19	3.061	23.8	3.89				Corroded
5.06	5.03	3.016	0.2		.03			Bright, smooth, unchanged
5.06	5.05	3.032	0.2			.03		Bright, smooth, unchanged
10.0	10.0	3.019	357.7	59.3				Corroded
10.2	10.2	3.015	377.4		62.6			Corroded
10.2	10.2	3.008	112.7			18.7		Corroded
10.0	10.0	3.000	0.9				0.15	Smooth, faint dullness
10.1[b]	9.8	3.007	1.0				0.17	Bright, smooth
			1.1				0.18	Bright, smooth
10.1[b]	9.8	3.005	1.0				0.17	Bright, smooth
			1.2				0.20	Bright, smooth

[a] Original weight of specimen 2.9 to 3.2 grams.
[b] Each bottle had 2 specimens.

1 N hydrochloric acid, corrodes slightly in 3 N acid, faster in 5 N, and rapidly in 10 N acid. The substitution of helium for air increases the corrosion rate in 1 and 3 N acid markedly but has relatively little effect in 5 and 10 N acid solutions. Although in helium atmosphere the change in electrode potential between 1 and 10 N acid is less than 0.1 volt, the change in corrosion rate is about 200-fold. Under the conditions used in these experiments, 2 milligrams of copper per liter is sufficient to prevent corrosion in acid concentrations up to 5 N in either air or helium and 20 or 200 milligrams of copper prevent corrosion in 10 N acid in either atmosphere.

Specimens that were not corroded retained their bright, smooth appearance at the end of the experiments. No change in the original appearance of the titanium could be detected by visual examination.

Specimens that were slightly corroded became dull or tarnished and those that corroded rapidly took on the unmistakable corroded appearance. Corrosion was always uniform, without sign of pitting.

Spectrographic analyses and spectral x-ray analyses did not show significant differences between the copper contents of titanium specimens immersed in 10 N HCl, 200 milligrams copper per liter, helium atmosphere for 3 days and specimens that were not immersed.

ADDITIONAL EXPERIMENTS ON PASSIVITY OF TITANIUM

Stagnant Solutions of Hydrochloric Acid

The passivity of titanium sometimes breaks down in very strong hydrochloric acid solutions even with high concentrations of copper present. This loss of passivity appears to be initiated in sheltered areas, such as the space under a glass sleeve with an imperfect glass seal. It was, therefore, decided to study this phenomenon by carrying out experiments in stagnant solutions. The experimental methods used were the same as those described earlier, except for the passage of helium or air through the solutions.

The electrode potential of titanium in a stagnant solution of 10 N hydrochloric acid with 200 milligrams of copper per liter is nearly the same as it is with circulating gases. After 1970 minutes of immersion the electrode potential was 0.57 volt, after 6435 minutes 0.53 volt, and after 8960 minutes the potential was -0.38 volt and the specimen was corroding rapidly.

Corrosion tests were carried out in loosely covered vessels. The specimens were always 3.38 inches long, 0.25 inch wide, and 0.05 inch thick but the solution volumes varied from 400 to 10 milliliters. The data summarized in Table 19 indicate that the solutions in which titanium is passive are the same with or without the passage of air or helium. However, when titanium is in contact with a small volume of stagnant 10 N

Table 19 - Passivity of Titanium in Stagnant Hydrochloric Acid Solutions

Solution		Volume per 2 sq. in. sample, ml.	Duration of passivity days	Time, days	Weight loss	
Normality	Copper ml./liter				Total, mg	Mg. per sq. inch per day
10	none	400	.00	3.502	544.5	77.1
	2	400	.00	3.545	564.8	79.6
	20	400	.00	3.545	473.7	66.7
	200	400	> 37			
		75	> 2.1 < 2.9			
		25	> 1.3 < 2.0	2.443	58.9	
		10	> 0.1 < 0.3			
5	none	400	.00	3.538	27.1	3.83
	2	400	.00	3.540	34.1	4.80
		25	.00	2.406	18.7	3.88
	20	400	> 37			
		25	> 27			
		10	> 12			
	200	400	> 37			
		25	> 27			
1	none	400	> 37			
		25	> 27			
	2	400	> 37			
	20	400	> 37			
	200	400	> 37			

[a] Conclusion based on lack of gas evolution, appearance of metal, bright surface.

hydrochloric acid containing 200 milligrams of copper per liter its passivity breaks down and the time required for the loss of passivity varies from approximately 0.2 day for 10 milliliters of solution to 2.5 days for 75 milliliters. This does not seem to occur in 5 N acid. The loss of passivity may be related to the accumulation of some reaction product in the solution, possibly atomic hydrogen. It should be noted that the passage of ordinary commercial hydrogen through 10 N acid containing 200 milliliters of copper per liter does not bring about the precipitation of copper and that metallic copper dissolves in this solution with the evolution of a gas. This is not in agreement with the position of copper in the E.M.F. series and is probably the result of low copper ion concentration caused by formation of a complex with hydrochloric acid.

Effect of Copper Ions in Sulfuric Acid Solution

A few brief, qualitative experiments indicated that the copper ion also has a passivating effect on titanium in sulfuric acid solutions. For example, polished or unpolished titanium begins to evolve gas after a few moments immersion in pure 64 percent sulfuric acid at 50° C. but there is no gas evolution if the solution contains 200 milligrams of copper per liter.

Hydrogen Atmosphere

Electrode potential measurements made with ordinary commercial hydrogen flowing through the electrolyte indicates

that this gas has the same effect as helium. In pure 1 N hydrochloric acid the electrode potential of titanium reached -0.11 volts in 192 minutes andin 10 N hydrochloric acid containing 200 milligrams copper per liter it was 0.55 volts after 224 minutes of immersion.

Melted Titanium

The results of experiments carried out with specimens of melted[a] titanium indicated that its passivity characteristics were similar to those of metal made by powder metallurgy technique. The metal used in this work contained the following impurities: carbon 0.11 percent, iron 0.15 percent, manganese 0.01 percent, silicon 0.01 percent, magnesium 0.005 percent, chlorine 0.02-0.08 percent, nitrogen 0.018 percent. In pure 1 N hydrochloric acid the electrode potential was -0.24 volt after 1434 minutes immersion in helium and 0.08 volt after 1164 minutes in air. The corrosion rate in pure 5 N hydrochloric acid was 6.3 milligrams per square inch per day for a 3-day test while the addition of 20 milligrams of copper per liter decreased the corrosion rate to 0.03 milligrams per square inch per day.

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[a] Made by Allegheny Ludlum Company.

EFFECT OF PASSIVITY OF TITANIUM ON GALVANIC CORROSION

A series of experiments carried out to study the corrosion of titanium-copper couples in various concentrations of hydrochloric acid in the presence of helium or air are included here to show the effect of the passivity of titanium on its galvanic behavior. In each test weighed strips of copper and titanium were coupled through a calibrated resistance, and together with identical, uncoupled specimens of each metal, were maintained in contact with hydrochloric acid solution in a sealed bottle. Voltage drops across the calibrated resistance and the electrode potentials of the couple and of the uncoupled specimens were determined at intervals during the experiment; weight changes were obtained at the end of each experiment.

The bottles used in these experiments were approximately 5 inches high and 3-1/2 inches in diameter, had a volume of 600 ml., and contained 450 ml. of electrolyte. The rubber stoppers had openings for gas inlet and outlet, the tube to the potassium chloride bridge, and 4 sample tubes. The metal specimens were 6-1/2 inches long and 1/4 inch wide, the titanium being 0.04 inch thick and the copper 0.065 inch thick. These were protected at the solution lines by enclosing them in wax filled glass tubes which passed through the stopper and extended to a point below the solution line, forming gas tight seals and permitting external electrical connections without solution line effects. The submerged sections were 2.75 inches long and 0.25 inch wide. The electrode potentials were measured and the solutions were prepared in the manner described before. The air was

passed through 3 percent sodium hydroxide solution and several water bottles before going to the specimen bottle and the 99.97 percent pure helium was passed through a water bottle. Neither gas was passed through preliminary acid bottles since this is unnecessary with acid more dilute than 5 N. The titanium metal used in these experiments was prepared in U. S. Bureau of Mines laboratories from powder containing 0.5 percent cobalt in addition to the usual impurities. Although the presence of cobalt may change the corrosion characteristics of the metal, it is considered satisfactory for these experiments. The copper was Revere Mixture 100, also known as Electrolytic or Tough Pitch copper, with a minimum of 99.9 percent copper; the copper specimens were not annealed. Titanium and copper specimens were prepared as described before.

Air or helium was passed through the solution for about one hour prior to, and continuously during, each experiment. After immersion of the metal specimens, one or more electrode potential measurements were made, and then the switch in the galvanic couple circuit was closed and the couple experiment started. The tests were made at room temperature, 23° to 28° C., and the length of the tests varied from 19 to 100 hours, depending on the corrosion rate. At the end of the experiment the specimens were removed from the tubes, cleaned, and weighed.

The metal lost from the specimens by galvanic corrosion was obtained by subtracting the weight loss of the uncoupled specimen from that of the coupled specimen of the same metal, upon the assumption that each undergoes the same chemical corrosion. This value was used to obtain the "calculated galvanic

current" by means of Faraday's Law. The "measured current" was obtained from the known resistance (.619 or .627 ohms) and the voltage drop across it. The copper content of the electrolyte at the end of the experiment was estimated from the total copper dissolved and the volume of electrolyte. Analyses proved that the flow of helium under the conditions of these experiments did not change the acid concentration appreciably. For example, the flow of helium through 2.95 N solution for 73.4 hours lowered the concentration of hydrochloric acid to 2.89 N. The consumption of acid resulting from metal solution was negligible in experiments with helium atmospheres and relatively large in air atmospheres. Percentage of original acid consumed is as follows (calculated from copper dissolved): No. 2 - 24 percent, No. 5 - 19 percent, No. 7 - 7.7 percent.

The essential data are summarized in Tables 20 and 21. In general, the electrode potential of the couple is between those of the uncoupled metals and is much closer to the more electronegative of the two. In other words, the system is under anodic control.

In a helium atmosphere and acid concentrations from 0.96 to 4.48 N and in air and 4.54 N acid the electrode potential of titanium in pure acid is more electronegative than that of copper and titanium should corrode galvanically. However, in two instances 0.96 N He and 4.54 air, the copper corroded galvanically because the titanium became passivated by copper ions formed by solution of the copper strips. This may have been accidental in the case of 0.96 N He but not in the case of 4.54 air since copper is very likely to corrode with air present.

Table 20 - Galvanic Couple Experiments, Titanium-Copper

Experiment number	Normality of HCl	Gas	Final copper content, gms/l (estimated)	Electrode Potential vs. Hydrogen Electrode							
				Copper		Titanium		Couple		Titanium in pure HCl solution	
				Time,[a] hrs.		Time,[a] hrs.		Time,[a] hrs.		Time,[a] hrs.	
9	0.96	He	0.03	1.17	-0.11	1.13	0.09	1.03	coupled		
				23.18	-0.05	23.18	0.20	1.25	-0.09		
				102.35	0.01	102.35	0.34	102.35	0.01	43.0	-0.31
3	1.98	He	0.0007	0.23	-0.16	0.15	-0.00	0.30	coupled		
				2.15	-0.13	2.10	-0.01	0.33	-0.15		
				5.58	-0.12	5.58	-0.09	5.58	-0.21		
				17.65	-0.06	17.65	-0.29	17.65	-0.27	20.6	-0.34
4	2.95	He	0.0007	0.75	-0.20	0.74	0.01	0.78	coupled		
				2.15	-0.19	2.13	-0.26	2.15	-0.28		
				73.38	-0.18	4.47	-0.34	4.50	-0.31		
						46.37	-0.36	46.37	-0.34		
						73.38	-0.37	73.38	-0.34	24.0	-0.34
6	4.48	He	0.01	0.30	-0.22	0.30	-0.28	0.35	coupled		
				5.18	-0.19	0.42	-0.30	0.40	-0.25		
				70.5	-0.18	2.78	-0.37	2.83	-0.31		
						70.50	-0.39	70.50	-0.34	29.8	-0.37
8[b]	4.48	He	0.002	0.22	-0.22	0.18	-0.03	0.30	coupled		
						0.27	-0.22	0.35	-0.23		
								22.75	-0.34		
2	1.98	Air	15	0.40	-0.10	0.32	0.31	0.45	coupled		
				1.45	-0.06	1.13	0.45	1.43	-0.05		
				3.60	-0.04	3.44	0.53	3.63	-0.04		
				7.25	0.02	3.57	0.55	7.28	0.04		
				17.45	0.16	7.20	0.58				
						17.45	0.48	17.53	0.22	49.5	0.03
5	2.96	Air	18	0.25	-0.13	0.22	0.25	0.32	coupled		
				0.60	-0.11						
				2.55	-0.06	0.57	0.39	0.60	-0.09		
				8.37	0.03	2.52	0.55	2.58	-0.05		
				20.21	0.13	5.27	0.60	5.42	-0.02		
						8.33	0.61	8.40	0.05		
						20.21	0.50			52.3	0.06
7	4.54	Air	11	0.33	-0.16	0.28	0.29	0.45	coupled		
				0.88	-0.15	0.53	0.41	0.53	-0.15		
				6.00	-0.07	0.88	0.51	6.00	-0.06		
				16.73	0.04	6.00	0.62	16.73	0.05		
				22.77	0.05	16.73	0.55	22.77	0.05		
						22.77	0.52			42.8	-0.27

[a] Immersion time.

[b] There were no uncoupled specimens.

Table 21 - Galvanic Couple Experiments, Titanium-Copper

Experiment number	Normality of HCl	Gas	Time coupled, hrs.	Weight loss, milligrams[a] Titanium	Weight loss, milligrams[a] Copper	Current in couple, milliamps. Time, hrs.[b]	Current in couple, milliamps. Measured	Current in couple, milliamps. Calculated
9	0.96	He	101.68	A .2 B .2	A 9.1 B 7.1 2.0		.01 Cu -	.016
3	1.98	He	17.17	A .7 B .1 .6	A 0.0 B 1.5		.01 Ti -	.059
4	2.95	He	73.53	A 12.6 B 10.4 2.2	A 1.5 B 0.0	1.08 1.95 3.68 4.55 46.62 71.52	.016 .081 .21 .23 .19 .21 Ti-	.05
6	4.48	He	70.23	A 27.8 B 21.0 6.8	A 4.3 gain B 10.7 loss	0.37 2.82 3.18 5.01 20.43 70.37	.13 .86 .83 .42 .41 .44 Ti-	.16
8[c]	4.48	He	75.37	A 39.	A 1.4		.65 Ti-	.27
2	1.98	Air	19.63	A .4 B .3	A 42578 B 30609 11968	.54 3.30 7.07 19.00	.10 .70 6.70 97.0 Cu-	51
5	2.96	Air	19.28	A 0 B 0	A 51561 B 39309 12254	.63 5.27 8.20 9.20	.11 4.0 18.7 26.6 incomplete Cu-	53
7	4.54	Air	22.35	A 1.0 B .1	A 35640 B 19486 16155	.47 2.87 6.37 16.73 22.80	.13 .32 4.0 59.0 76.0	62

[a] A specimens were coupled; B specimens were uncoupled.

[b] Immersion time.

[c] There were no uncoupled specimens.

In those instances where the electrode potential of titanium is more electronegative than that of copper and the amount of copper in solution was too small to passivate the titanium, galvanic corrosion of titanium occurred as expected. In 1.98 air and 2.96 air copper is electronegative to titanium in pure acids and corrodes galvanically, but the rate of galvanic corrosion may have been increased by the passivation of the titanium. In general, the galvanic corrosion of copper is much more rapid than that of titanium. The exception was 0.96 N, He where copper corroded very slowly. This corrosion rate was slow because of much cathodic polarization because of lack of oxygen. The fact that the potentials of the coupledand the uncoupled copper strip are the same, 0.01 volt supports this explanation. In other cases where copper corroded galvanically the air supply was ample. It was observed in these experiments that changing the rate of air flow caused corresponding changes in the galvanic current but changes in the rate of helium flow had no effect. Furthermore, when titanium corrodes galvanically the current rises to a peak during the first few hours after the circuit is completed, then drops to a lower value and remains fairly constant during most of the experiment. On the other hand, when copper corrodes galvanically the current generally rises at a moderate rate during the first 5 to 7 hours and then rises very rapidly during the remainder of the test.

The measured and calculated "current in the couple" are generally of the same order of magnitude, indicating that a considerable portion of it is caused by metal solution. The

most notable exception to this generalization is in the case of 0.26 N acid, air where there is a large current without galvanic corrosion of copper. High chemical and galvanic corrosion generally occur together. An exception was observed in the case of copper in 4.54 N acid and air atmosphere where chemical corrosion is lowest and galvanic highest. Experiments 6 and 8 (4.48 N, He), in which the electrolytes contained relatively little dissolved copper, gave similar results indicating that the presence of uncoupled specimens had no effect under these conditions.

SUMMARY AND CONCLUSIONS

The data summarized in Table 22 show that air or low concentrations of certain dissolved metals passivate titanium in strong hydrochloric acid solutions and that passivity is accompanied by very noble electrode potentials. An electrode potential more electronegative than -0.25 volt seems to indicate the absence of passivity. In no instance was the electrode potential of a corroding specimen more electronegative than -0.4 volt, although the standard electrode potential for titanium has been calculated as -1.75 volt from thermodynamic data. The results of a few experiments carried out with specimens of melted titanium indicate that this metal exhibits the same type of passivity. When titanium specimens are placed in contact with small volumes of solution containing 10 N hydrochloric acid and 200 milligrams of copper per liter with only limited contact between the solution surface and the outside atmosphere and there is no gas bubbling through the solution, passivity breaks down after a period of time. This time interval seems to be proportional to the ratio of solution volume to specimen area being about 0.2 day for a solution volume of 10 ml. per 2 square inches of specimen surface area and more than 2 days for 75 ml. per 2 square inches. This loss of passivity does not occur, or occurs much more slowly, with 5 N acid containing 200 milligrams of copper

Table 22 - Passivity and Corrosion of Titanium

Electrolyte	Passivity		Corrosion	
	Concentration and gas flow	Electrode potential,[a] volt	Concentration and gas flow	Electrode potential,[a] volt
HCl, pure	1 - 3 N, air	0.05	4 - 10 N air	-0.27 to -0.40
			1 - 10 N He	-0.31 to -0.39
HCl, 0.003 mole per liter dissolved metal[b]	1 N air or He	0.04 to 0.90		
HCl, 0.003 mole (200 mg) dissolved copper per liter	1 - 10 N air or He	0.40 to 0.65		
HCl, 20 mg. dissolved copper per liter	1 - 10 N air	0.45 to 0.55		
	1 - 5 N He	0.48 to 0.55	10 N He	-0.40
HCl, 2 mg. dissolved copper per liter	1 - 5 N air	0.43	10 N air	-
	1 N He	0.43	5 - 10 N He	-0.38
NaCl	1 - 3% open	0.35		
H_2SO_4	1.1 N open	0.20	2.2 N open	-0.33

[a] Steady-state potential referred to normal hydrogen electrode.

[b] Gold, copper, platinum, iron, mercury, zinc, cobalt, aluminum, magnesium

per liter. The loss of passivity is attributed to the accumulation of atomic hydrogen. However, passivity appears to be maintained if commercial hydrogen is substituted for helium or air.

Although the more noble electrode potentials indicate that a reaction involving oxygen, metal-yl or metal ions takes place at a passive surface, there is no visible deposit on or change in the appearance of the surface except for a slight tarnish in certain borderline solutions. These ions may be called passivators or anodic inhibitors and the system is apparently under anodic control. The tendency for titanium to be passivated by these ions should affect the galvanic behavior of titanium as was demonstrated with copper-titanium couples in hydrochloric acid solutions. Titanium is also passive in dilute solutions of sodium chloride in contact with air but the effect of air was not studied in this case. Titanium is passive in 1.1 N solutions of sulfuric acid in contact with air but not in 2.1 N acid. Dissolved copper also produces passivity in sulfuric acid solutions.

The passivity and noble electrode potential exhibited by titanium metal in 1 to 3 N hydrochloric acid solutions with air bubbling through the solution may be attributed to the existence of a thin, invisible layer of an oxygen compound of titanium on the surface. Presumably, the film requires oxygen for repair and is dissolved faster than it can be repaired in acid stronger than 3 N. Hence, passivity breaks down in helium atmospheres and in acid stronger than 3 N.

In acid solutions titanium has a strong tendency to form Ti^{2+} ions and purple Ti^{3+} ions with the liberation of atomic hydrogen.[a] Copper ions, when present in the solution, may precipitate on large areas of the titanium surface forming an invisible film of inactive titanium-copper alloy and thus tend to stifle the formation of titanium ions. It is well known that titanium forms alloys with copper[1,46] as well as with most other metals[10,32,33]. Although no copper was detected on the surface of the specimen by physical methods, this assumption seems justified by the more noble electrode potential and the lower corrosion rate. Furthermore, the increase in electrode potential produced by the various metals is related to their nobility. In 10 N hydrochloric acid the tendency for titanium to dissolve may be greatest and perhaps the passivating effect of copper is decreased by more complex ion formation. This would increase the rate of formation of atomic hydrogen. The greater quantity of atomic hydrogen will have no effect on the passivity if it is swept from the solution by the passage of a gas. But if the solution is stagnant and the volume relatively small, sufficient hydrogen can accumulate to destroy passivity. In 5 N acid the tendency for titanium to dissolve is less and the effective concentration of copper ions may be greater so that the loss of passivity occurs very slowly, if at all.

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[a] $Ti = Ti^{++} + 2e^-$ $\quad E^o = -1.75$ volts
$Ti^{++} = Ti^{+++} + e^-$ $\quad E^o = -0.37$ volts

(Latimer p. 251)

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